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AN INVESTIGATION ON MICROHARDNESS STUDIES OF THE PURE AND ALKALI METAL HALIDE DOPED POTASSIUM DIHYDROGEN PHOSPHATE CRYSTALS

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Abstract- *Pure potassium dihydrogen phosphate (KDP) crystals and KDP doped with sodium chloride (NaCl) and potassium chloride (KCl) have been grown by slow evaporation technique at room temperature. The grown crystals have been investigated using powder X-ray diffraction (XRD) and microhardness measurement techniques. The XRD studies are indicative that KCl and NaCl has been doped in KDP and the prepared materials are crystalline solids and a clear distortion has been observed in the doped crystals. Hardness of the crystals is dependent on the presence of dopants in the crystals and load dependence hardness has been found for all the alkyl halide doped KDP crystals. Microhardness studies have revealed that the dopants have affected the hardness value of the material. The work hardening index (n) or Meyer's index has demonstrated that the doped crystals are moderately harder materials. It has also revealed that the dopants have affected the hardness value of the prepared doped crystals. The detailed results of the hardness parameters have been discussed.*

Keywords: KDP, Alkali metal halide, XRD, Microhardness.

1. Introduction

KDP is a negative (doubly) double refracting crystal used for harmonic generation. KDP crystals doped with metal ions show a good non-linear optical property. Due to thermal and mechanical effects, KDP's performance as a photonic material has been limited. Scientists have shown keen research interest towards improving its mechanical properties through doping. The hardness test measures the resistance to penetration of the surface of a material by a hard object. Hardness, being the essential solid state property of any material, accuracy of hardness parameter has a significant importance in mechanical engineering, materials science and engineering, ceramics engineering towards manufacturing of machineries, tools, implants, bio-materials and ceramics products. Notwithstanding we expect that a constant hardness value for a particular material, a load dependence hardness value have been found in all experiments. Of more crucial importance, the hardness value has been found to be varied with the load even on the same surface of the material measured at some regular interval of distances. Therefore, it has become important to know the exact hardness value of a material to be suitable from the application point of view. A variety of hardness tests have been advised, but the common hardness tests include [1], Brinell test, Rockwell test, Knoop test and Vickers test. However, from the physical point of view, the hardness is the resistance offered by the crystal for the movement of dislocations and practically it is the resistance offered by the crystal for localized plastic deformation [2] and hardness testing provides useful information about the mechanical properties like elastic constants, yield strength etc. The Vickers test is the micro-hardness test and it forms such small indentations that a microscope is required to obtain the measurement. The hardness is utilized mostly as a basis for comparison of materials, specifications for manufacturing and heat treatment, quality control, and correlation with other properties and behavior of materials [1].

The mechanical functioning of materials is characterized by their mechanical properties and the hardness test, besides providing a measure of the wear and abrasion resistance of the material, can be correlated to a number of other mechanical properties like elastic constants and can furnish information on strength and deformation characteristics [3] such as lattice destruction or the resistance offered to permanent deformation or damage [4].

A standard applied material for second harmonic generation (SHG) is KDP which is a negative (doubly) double refracting crystal [5]. The various applications of

KDP crystals have created a research thirst among the scientists towards improving its mechanical properties so that it could be suitable from the application point of view [6].

Earlier researchers have characterized chemical, optical and spectroscopic parameters and have been measured after doping metal 3+ ions such as Ce^{3+}, Sm^{3+}, Gd^{3+} and Yb^{3+} utilizing metal organic complexes of rare-earth metals or metal salt solutions [7] but their mechanical properties are yet to be examined. Notwithstanding a number of works has been reported on physical properties like elastic constants, thermal expansion etc. but a negligible amount of information is available on hardness which is considered as an important strength parameter [2].

The use of KDP as a photonic material in the third harmonic generation to reduce light wavelength from 1.054 µm to 351 nm has been constrained due to its susceptibility to laser damage, a process that couples light absorption with thermal and mechanical effects [2]. To overcome this problem associated with KDP scientists have been taking attempts to provide an insight into this problem. A class of such crystals has been grown from their supersaturated solution in distilled water, during a slow cooling process. It has been reported that a good number of researchers have doped KDP crystals by KI, NaI and Au^{+}, ammonium compounds, urea and thiourea towards characterization and obtaining exact information about this [8]. The identification of new types of functional materials has become a challenge for the researchers of this emerging arena of nonlinear optics [9]. KDP crystals doped with metal ion impurities have better non-linear optical property with compared to pure KDP crystals [6]. A class of such crystals, Potassium dihydrogen phosphate (KDP), KH_2PO_4 doped with NaCl and KCl has been grown from their supersaturated solution in distilled water, during a slow cooling process in our present research program.

Organic doped Crystals are economical from cost of point of view. They show fast and large non-linear response over a broad frequency range. Besides, they possess inherent synthetic flexibility, high optical damage threshold and intrinsic tailor-ability [9]. They possess less thermal and chemical stability and small mechanical hardness [9]. But **i**t has been found that the molecules in pure organic crystals are often bonded by weak Van der Waals forces of hydrogen bonds which result in poor mechanical and they possess less thermal and chemical stability.

Recently it has been revealed that the inorganic doped crystals, i.e., KDP doped with NaCl and KCl are good in thermal stability and moderate in mechanical hardness [10]. Moreover, they can show second order nonlinear optical properties, and can be grown in large size high quality single crystals those show a small non-linear response over a broad frequency range [9]. It may be mentioned here that a very few research papers on characterization on metal halide doped KDP crystals are available. In our present investigation, influence of metal halide such as KCl and NaCl dopants on the mechanical and physical have been studied systematically.

1.1 Chemical composition of the prepared sample crystals

In the present research study, the pure.KDP, M=136.09gm/mol, Assay (Acidian) Cal c.a.d.s. 98-100, PANREAC QUIMICA SAU, Spain, KCl, M=74.55 gm/mol, MERCK, India, Assay (KCl) ≥ 99% and NaCl, M=58.44 gm/mol, Assay (NaCl) ≥ 99%, MERCK, India have been procured from a commercial supplier towards preparation of pure and alkyl halide doped potassium dihydrogen phosphate crystals.

1.2 Sample preparation

At the very beginning, a stock solution of 2.5 molal solution of analytical grade KDP (KH_2PO_4), KCl and NaCl have been prepared and have been reserved in three different beakers. Traditional Chemical process has been followed for the preparation of the 2.5 molal mother solutions. Analytical grade KH_2PO_4, NaCl, KCl and distilled water have been used for growth of single crystals by the slow evaporation method. Parent material KDP and dopant alkyl halides viz. NaCl and KCl are mixed in different volumetric ratios 35, 45, 85 ml with the fixed 50 ml of KDP solution. The solutions have been stirred long enough to ensure complete dissolution of the solute and then filtered. The prepared stock solutions have been kept at room temperature. Pure KDP crystals from 2.5 molal aqueous solutions have been prepared by natural evaporation and cooling method. The same method has been followed for the preparation of 2.5 molal KCl and NaCl solutions. Then the KCl and NaCl in different volumetric ratios (35, 45 and 85 ml) have been mixed with a 50 ml fixed of 2.5 molal mother solution of KDP. The mixture solutions have been thoroughly stirred for 6-8 h continuously for ensuring homogenization of the mixtures. The seed crystals have been harvested in the conventional manner, Fig. 1. The best seed crystals have been selected and have been placed in appropriate solutions for further growth of these single crystals.

Fig. 1: Seed crystals of 85 ml NaCl doped KDP crystal.

The vessels containing the solutions have been closed with perforated cover and have been kept at room temperature (~30^0C) to allow natural evaporation and cooling of the solvent.

Transparent good quality crystals were collected after 20 days Fig. 1. Single crystals of KCl and NaCl doped KDP started to grow about 8-10 days in the petri dishes and reach optimum size in 18-20 days and shown in Fig. 2. The grown pure and doped crystals are found to be transparent and free from defects. Single crystals with smooth surfaces have been selected for Vickers microhardness test.

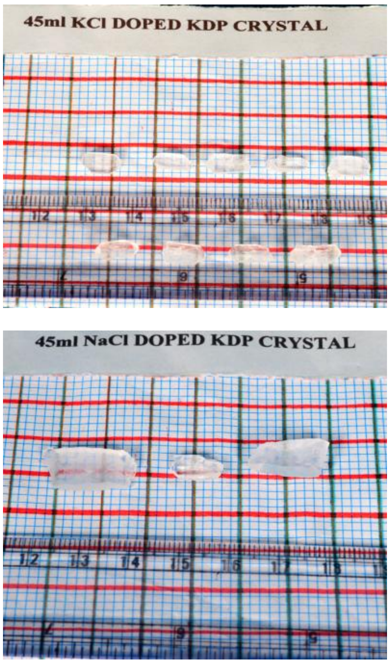


Fig. 2: Photographs of some prepared KCl and NaCl doped crystals.

1.3 XRD analysis of pure KDP, KCl and NaCl doped KDP crystals

The Bragg diffraction condition for X-rays is given by, which is known as Bragg diffraction law, after W.L. Bragg, $2d\sin\theta = n\lambda$. X-ray diffraction has been carried out for the prepared pure KDP crystal, KCl (35, 45 and 85 ml) and NaCl (35, 45 and 85 ml) doped KDP (50 ml) crystals using D8 Advance, Bruker AXS, Germany.

The X-ray patterns of X-ray powders of pure KDP, (35, 45 and 85 ml) KCl and NaCl doped crystals clearly suggest that these are constituted from the crystal or crystalline solids [11]. Therefore, the XRD spectra shown in Fig. 3 confirm that the prepared KCl and NaCl doped KDP materials are basically crystals [11]. All the samples show good crystallization with well defined diffraction lines. The sharp fundamental reflections from the Bragg planes indicate that the prepared pure KDP, KCl and NaCl doped crystals are of single phase. The positions of the peaks comply with the reported values [12]. A slight deformation of the doped crystals with respect to pure KDP crystal is mainly due to the strain on the lattice by doping of KCl and NaCl. Comparing the powder XRD pattern with the pure KDP, there is a small shift in the NaCl and KCl doped XRD of KDP. This confirms the incorporation of NaCl and KCl in the KDP crystal lattice.

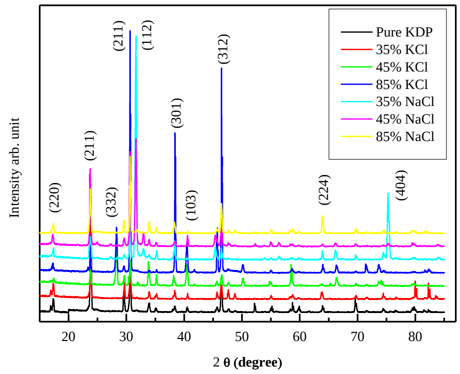


Fig. 3: XRD diffractograms of pure and doped KDPs.

1.4 Microhardness measurement of pure KDP, KCl and NaCl doped crystals

The most general measurement of hardness is the indentation type. The common definition of indentation hardness is the ration of the applied load to the surface area of indentation. The microhardness value is calculated using [2]:

$$H_V = 1.8544P/d^2 Kgmm^{-2} \qquad (1)$$

where H_v is the Vickers hardness number, P is the applied load (gm) and d is the diagonal length (mm) of the indentation.

The relationship between the load and size of indentation, has given by Meyer's law as:

$$P = ad^n, \qquad (2)$$

where P is the load in gm, d is the diagonal length of impression (diameter of the recovered indentation in mm) and 'a' and 'n' are constants for a given material. The Meyer index number n or called as work hardening index can be estimated from the slopes of the log p versus log d plots [2]. The value of n is expected to be 2 but most of the experimental data show that it is always less than 2. Onitsch and Hanneman have pointed out that n lies between 1 and 1.6 for hard materials and the values are more than 1.6 for softer materials [2].

The microhardness studies have been performed by Vickers indenter (Microhardness HMV 2T, Shimadzu Japan). The defect free crystals having flat surfaces have been selected for Vickers hardness measurement. To ensure the precise measurement of work hardening index (n), the instrument has been set for obtaining five readings for each of the applied loads (P). The average diagonal length of impression d and the average Vicker's hardness (H_v) have been evaluated for 10, 25, 50, 100 and 1961 gm, respectively.

1.4.1 Load variation of Vicker's microhardness

The load variation of hardness data for pure, KCl and NaCl (35, 45 and 85 ml) doped KDP crystals has been recorded. The observed load dependence is similar to the typical load dependence. To ensure the precise measurement of work hardening index, the instrument has been set to record of five readings for each of the applied loads. It has been observed clear load independence in all KCl and NaCl doped KDP crystals beyond a load of 25 gm for KCl and NaCl doped KDP crystals and beyond a load of 50 gm for pure KDP crystal. In hardness measurement, the major problem is the occurrence of microcracks with the passage of applied load. In the present case, the surface around the indentation have been affected by microcracks observed as white spots, these have been formed besides the cracks at the corners of impression. It is important to note that the microcracks around the impression occurred around a load of 50 gm only in KCl doped KDP crystals and they tend to increase with the increase of load, seen as long cracks at the corners and overshadow the region around it. This has caused difficulty in the precise measurement of the diagonals of the impressions at higher loads, especially beyond a load of 100 gm, both in KCl and NaCl doped KDP crystals. Therefore, we have excluded the hardness data beyond a load of 100 gm. For this reason, the hardness studies have been limited up to 1961 gm only. Due to this fact, a clear load independent region could not be obtained. Notwithstanding, a leveling trend has been observed from a load of 50 gm. To remove discrepancy in the hardness on these two types of doped crystals that might occur from mutual influence of scattering, the instrument has been calibrated at 10 vernier scale division interval for performing five separate indentation studies. In cases where a several number of hardness values are found to be observed the load independent values are considered to be just beyond the lowest value of that particular range [2]. Vickers hardness number with different applied for pure KDP are 154, 173, 185, 177, 186 kg/mm^2 but for 85 ml KCl doped KDP are 171, 194, 161, 141, 136 kg/mm^2, for 45 ml KCl doped KDP measured values are 106, 23.30, 36.30, 42.40, 93, 42.40 kg/mm^2 and for 35 ml KCl doped KDP are 104, 118, 169.80, 115, 106 kg/mm^2. In contrast, the measured Vickers Hardness Number for 35 ml NaCl doped KDP have been measured as 113, 105, 156, 87, 84.76 kg/mm^2, for 45 ml NaCl doped KDP as 127, 159, 156, 122, 115 kg/mm^2 and for 85 ml NaCl doped KDP as 141, 194, 168, 173, 144 kg/mm^2. In the present case, we can assume that most hardness values lie in the following ranges:

173-186 kg/mm^2	for pure KDP
104-118 kg/mm^2	for 35 ml KCl doped KDP
36.30-93.00 kg/mm^2	for 45 ml KCl doped KDP
136-141 kg/mm^2	for 85 ml KCl doped KDP
84.80-87 kg/mm^2	for 35 ml NaCl doped KDP
115-127 kg/mm^2	for 45 ml NaCl doped KDP
141-168 kg/mm^2	for 85 ml NaCl doped KDP

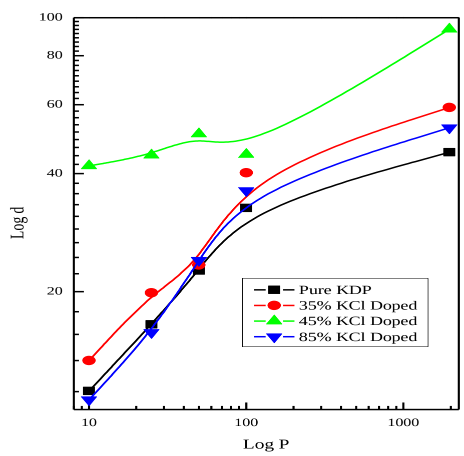
By applying the same sense of logic, the above results suggest that the load independent hardness values are: 174 kg/mm^2 for pure KDP, 105 kg/mm^2 for 35 ml KCl doped KDP, 38 kg/mm^2 for 45 ml KCl doped KDP, 137 kg/mm^2 for 85 ml KCl doped KDP, 86 kg/mm^2 for 35 ml NaCl doped KDP, 116 kg/mm^2 for 45 ml NaCl doped KDP, 142 kg/mm^2 for 85 ml NaCl doped KDP. Several researchers have found several hardness values for pure KDP crystals. Now, in comparison with the earlier results, shows that the present hardness value for pure KDP is higher than the earlier reported values. However, the present hardness value of 174 kg/mm^2 is approximately close to the previous reported value of 166 kg/mm^2 for pure KDP. On the other hand, as we have no sufficient hardness data on KCl and NaCl doped KDP crystals for these particular volumetric ratios, we could not compare the experimentally obtained data for those crystals. However, our experimental data will enrich the existing data library and further studies could be performed for confirming the genuineness of the evaluated data towards obtaining the exact hardness information of the mentioned prepared doped KDP crystals. It has been reported that the crystal with less Vicker's hardness produce moderately good impressions and this due to the less brittle nature of the crystals wherein the crystals with higher Vicker's hardness values develops rough impressions or more cracks and this is occurred because of the more brittle nature of the crystal [2]. As the Vicker's hardness values for all the KCl and NaCl doped prepared crystals have been found to be moderately lower values , the prepared crystals will be less brittle and would be better from the second, third, fourth and fifth harmonic generation and communication point of view towards resolving the breakdown problem or laser damage threshold of the KDP crystals.

1.4.2 Log p Versus Log d Plots

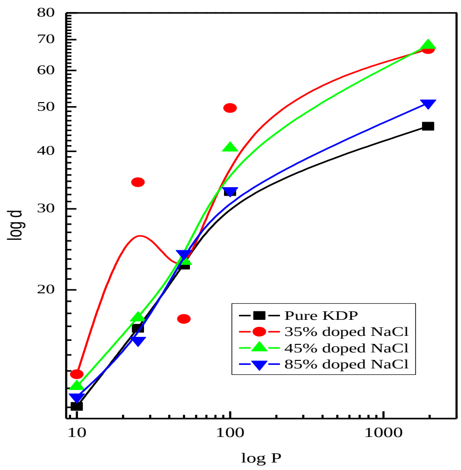
The figures for pure, KCl and NaCl doped KDP have been showing an agreement with the Meyer's Law up to a load for 100 gm in the Log p Vs Log d plot.

Meyer Index number (n) or work hardening index have been estimated from the slopes of the respective graph for each of the doped crystals. The value of 'n' is expected to be 2 but most of the experimental data provides evidence that it is always less than 2 [2]. Onitsch and Hanneman pointed out that 'n' lies between 1 and 1.6 for soft materials [2].

The 'n' values observed in the present studies have been found well below 1.6 indicating that pure, KCl and NaCl doped KDP crystals are moderately harder substances.



(a)



(b)

Fig. 4: Variation of log p versus log d for (a) KCl doped KDP (b) NaCl doped KDP

Hardness of the crystals is dependent on the presence of dopants in the crystals. Prepared crystals have been found to be moderately harder materials showing different Meyer's indexes.

2. Conclusion

From the XRD studies it can be inferred that KCl and NaCl has been doped into the KDP crystals and distortion due to doping has been observed in the crystals. The Vicker's hardness value H_v for pure KDP is 174 kg/mm^2, for 35, 45 and 85 ml KCl doped KDP are 105 kg/mm^2, 38 kg/mm^2 and 137 kg/mm^2, and those for 35, 45 and 85 ml NaCl doped KDP are 86 kg/mm^2, 116 kg/mm^2 and 142 kg/mm^2, respectively. Moreover, the research findings are indicative that the doped crystals are moderately harder materials. Finally, it would enrich information about metal halide doped KDP crystals by integrating the existing data library and help the future researchers towards preparing super quality crystals to be used for desired harmonic generation, laser application and communication point of view as well.

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Nomenclature

Symbol	Meaning	Unit
d	Interplaner spacing	(m)
θ	Angle	(°)
n	Order	-
λ	Wavelength	(nm)
H_v	Vickers hardness number	Kgmm^{-2}
P	Applied load	(gm)