Optical and Structural Characterization of Doped KDP Crystals

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Abstract- *Crystals of potassium dihydrogen phosphate (KDP) doped with Ethylene Diamine Tetra Acetic Acid (EDTA) and Methyl Violet (MV) were grown by slow solvent evaporation method at ambient temperature. The good quality single crystals were grown in 21 days. The presence of EDTA and Methyl Violet was confirmed by EDAX. The lattice parameters of the single crystals were recorded by single crystal X ray diffraction. The optical nature of the grown crystals was analyzed using the UV-Vis spectrum. The hardness of the crystal has been determined.*

Keywords- KDP, EDTA, Micro hardness, single crystal.

I. INTRODUCTION

KDP is among the most popular NLO material. It is characterized by rich UV transmission, high damage threshold even though their NLO coefficients are relatively low. In addition they are also excellent electro – optic crystals used as pocket cells, Q switches and several other applications. Various techniques have been tried to increase the growth rate and improve the NLO properties of the KDP crystal. Improvement of the quality and performance of KDP based devices can be achieved with suitable dopants. This improvement was achieved by doping Ethylene Diamine Tetra Acetic Acid (EDTA) and Methyl Violet in KDP crystals, which were grown by slow evaporation technique at ambient temperature. Recent studies on doping of KDP crystals with several dyes with different concentrations of impurities such as Chicago Sky Blue, Sunset Yellow, Amaranth shows that it could change the lattice parameter of KDP crystals and introduce some deformation which cause the changes in their optical properties. The purpose of the study is to investigate the influence of EDTA and Methyl Violet with different concentrations on growth, morphology, crystalline habits, optical properties and hardness of KDP crystals.

II. METHOD OF EXPERIMENT

Single crystals of pure KDP and doped KDP were grown by slow evaporation of the saturated aqueous solution at room temperature. Analytical reagent grade (AR) samples of Potassium dihydrogen phosphate and methyl violet and EDTA were used as dopant for synthesis of the crystal. A super saturation solution of potassium dihydrogen phosphate was prepared in triple distilled water filtered out in a petri dish. After a period of two weeks, transparent colorless seed crystals of various sizes were harvested. The super saturated KDP solution of 400ml was prepared, filtered and a seed crystal of KDP was allowed to grow with slow evaporation technique at room temperature for 21 days. In a similar way the super saturated KDP solution with the EDTA as dopant and another dopant with various concentration of methyl violet viz 0.1mol% and 0.2mol% were prepared in triple distilled water and seed crystals of KDP were allowed to grow with slow evaporation method for 21 days. The photographs of the as grown KDP crystal and doped KDP crystals are shown in figures below.

Pure KDP crystal

0.1mol% MV doped KDP crystal

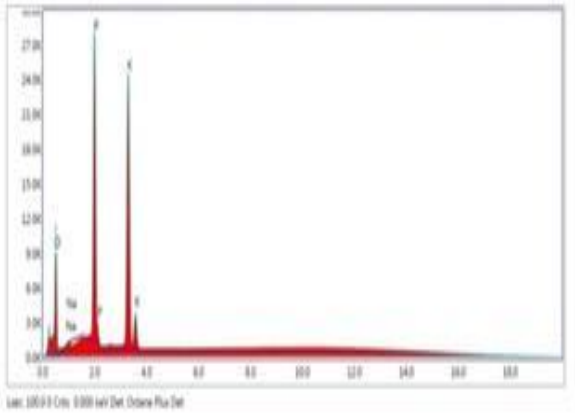
0.2mol% MV doped KDP crystal

EDTA doped KDP crystal

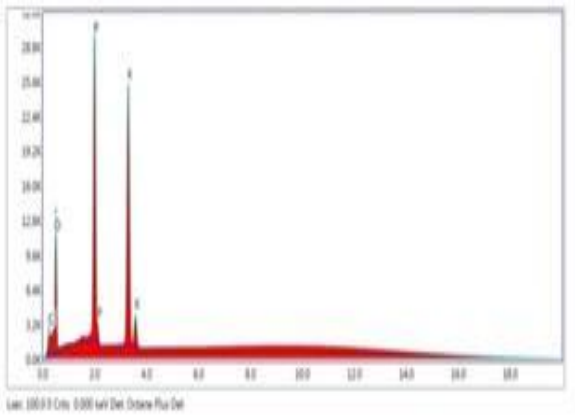
III. RESULTS AND DISCUSSIONS

A. EDAX analysis

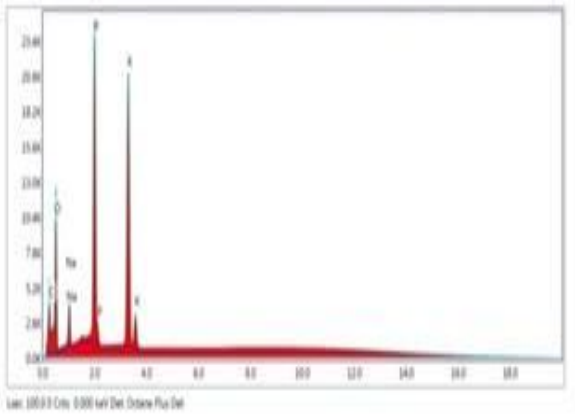
In order to confirm the presence of functional group, the sample of grown crystals was subjected to EDAX analysis. The EDAX spectra for pure and 0.1mol% and 0.2mol% of methyl violet and EDTA doped KDP crystals were recorded and analyzed. From the spectrum of pure crystals it is clear that there is no peak other than that of potassium and phosphate, as expected from pure KDP crystals. The presence of carbon in KDP crystalline lattice it proves that crystal violet dye and EDTA presence in the crystal. The recorded EDAX spectrum is shown below. The observed weight percentage of elements in the pure KDP and boron doped KDP crystals are given in the table below. As we increase the mol% of crystal violet dye in solution it leads to increase the weight% and atomic% of carbon.



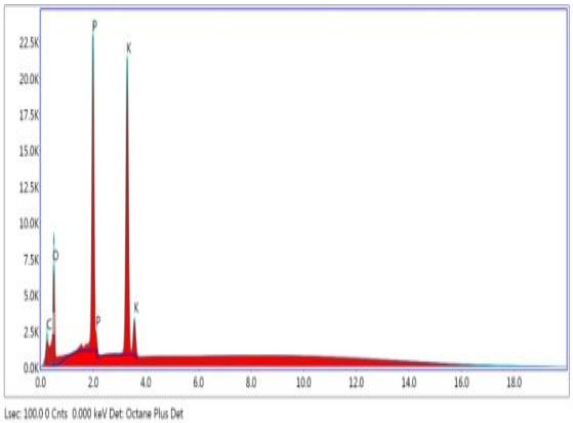
Graph1: PURE KDP CRYSTAL



Graph 2: 0.1mol% MV DOPED CRYSTAL



Graph 3: 0.2 mol% MV DOPED CRYSTAL



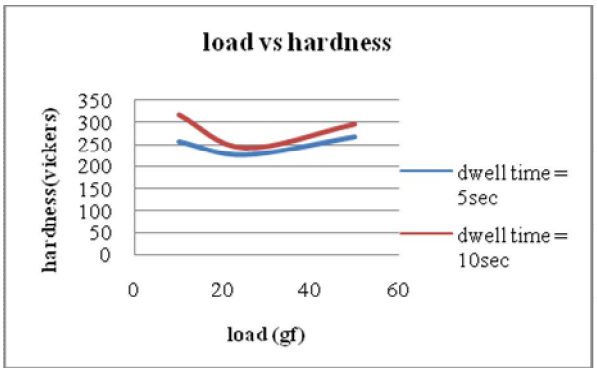
Graph 4: EDTA DOPED CRYSTAL

Element	Pure KDP		0.1% MV		0.2% MV		EDTA	
	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
C	-	-	5.10	9.01	16.62	26.49	6.55	11.66
O	45.98	64.93	46.66	61.84	41.04	49.11	43.41	58.01
Na	1.03	1.02	-	-	4.50	3.75	-	-
P	22.65	16.52	21.10	14.44	16.55	10.23	20.72	14.30
K	30.34	17.53	27.14	14.71	21.28	10.42	29.32	16.03

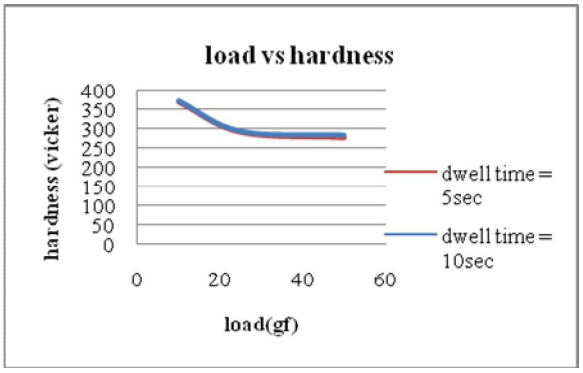
B. Micro hardness studies

Micro hardness of a crystal is its capacity to resist indentation. The hardness of a material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. To evaluate the Vickers hardness number, an indentation time of 5 sec and 10 sec was applied on the (100) face of the crystal for various loads.

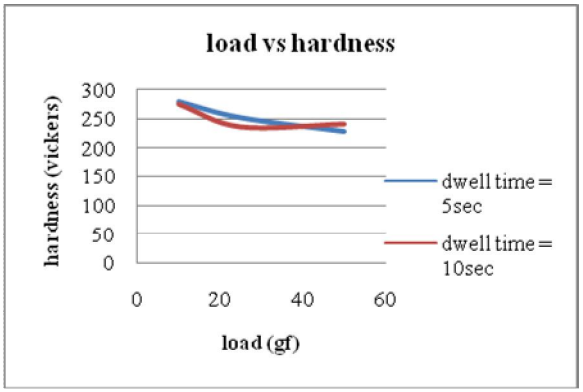
Hardness test is useful to find the mechanical hardness of the crystal and to estimate the threshold mechanical stress. Vicker's hardness measurement of pure and doped KDP crystals were noted by applying loads of 10g, 25g and 50g for an indentation time of 5 sec and 10 sec for each trial. Repeated trials were performed to ascertain the correctness of the observed results. The collected data is presented in Tables below. The Vickers's microhardness number (Hv) was calculated using the relation Hv=1.8544 P/d2 (kg/mm2), where P is the indenter load in kg and d is the diagonal length of the impression in mm. The plot of Vickers hardness versus load for the pure and doped KDP crystals is shown below. From the graph it is seen that the hardness value of the KDP crystals varies with the doping, whereas in case of EDTA doped KDP crystals it decreases.



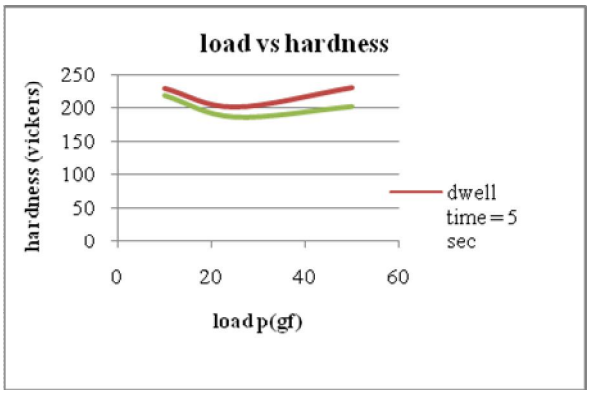
Graph 1: Pure KDP Crystal



Graph 2: 0.1% MV Doped Crystal



Graph 3: 0.2% MV Doped Crystal

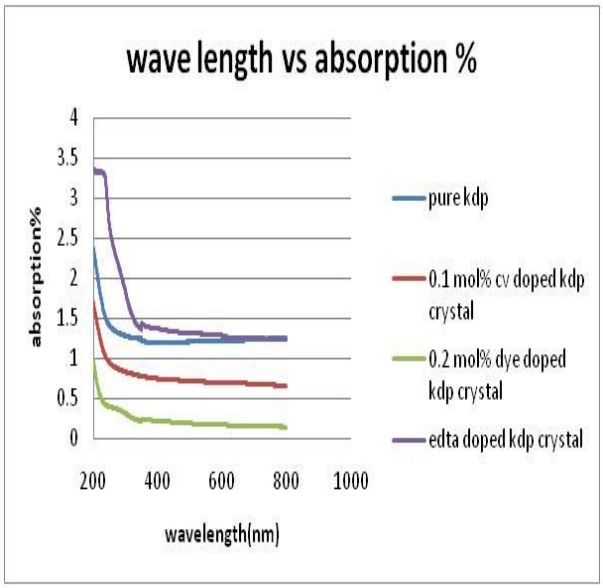


Graph 4: EDTA Doped Crystal

Hardness conversion depends on material type and characteristic. The average microhardness of different crystals from graphs are Pure KDP crystal is 266.94 vickers, 0.1mol% crystal violet doped KDP crystal is 314.08 vickers, 0.2mol% methyl violet doped KDP crystal is 252.22 vickers, EDTA doped KDP crystal is 211.36 vickers. The microhardness of 0.1mol% crystal violet doped KDP crystal are found to be higher than the pure KDP crystal, 0.2mol% crystal violet doped KDP crystal are found to be less than the 0.1mol% crystal violet doped KDP crystal and EDTA doped KDP crystal are found to be less than the pure KDP crystal.

C. UV-Vis Analysis

UV-Vis spectra show that the grown crystals are optically transparent through 200-800 nm and hence suggests the suitability of this material for optical devices. As the wavelength increases it leads to decrease percentage of absorption for each crystal. On increasing the percentage of methyl violet dye in the crystals of KDP the percentage of absorption decreases. Lower wavelength absorption is higher in EDTA doped KDP crystals than that of Methyl Violet doped KDP crystals.



The detailed graphical analysis of absorption at different wavelengths and intercept of straight line on the wavelength λ and optical energy band gap Eg for all crystal are shown below:

Sr.no	Sample	The intercept wavelength λ(nm)	Optical energy band gap Eg (ev)
1	Pure KDP	301	4.11
2	0.1 mol%CV doped KDP crystal	272	4.55
3	0.2 mol%CV doped KDP crystal	238	5.20
4	EDTA doped KDP crystal	324	3.83

IV. CONCLUSION

Potassium dihydrogen phosphate doped methyl violet dye and EDTA crystal was grown by solution evaporation technique to enhance the physicochemical and optical performance. The EDAX analysis shows the presence of carbon in KDP crystalline lattice confirms the presence of violet dye and EDTA in the crystal. The microhardness of the crystal tested by Vicker's hardness tester shows that the hardness value of the KDP crystals varies with the doping, whereas in case of EDTA doped KDP crystals it decreases. Also UV-VIS spectra shows that the grown crystals are optically transparent through 200-800 nm and hence suggests the suitability of this material for optical devices. This study may prove to be helpful to obtain high quality single crystals for various applications.

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