Effect of Magnesium Chloride on the Habit Modification of Spectral, Thermal and Nonlinear Optical Properties in KDP Crystals

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Abstract— The additive of magnesium chloride with potassium dihydrogen ortho phosphate (KDP) modifies some of its spectral, thermal, hardness, linear and nonlinear properties. The nonlinear optical single crystal of pure and magnesium chloride added KDP was grown by slow evaporation method. Single crystal X-ray diffraction study shows that it belongs to tetragonal system. FTIR spectral analysis was carried out on the material to validate the presence of functional groups. UV visible spectra was recorded for the samples to analyze the transparency in visible and near Infrared (NIR) region. Atomic absorption study reveals the presence of additives in the crystal. The thermal stability has been analyzed by using TG/DTA studies. The Microhardness analysis of the grown crystals was studied. Its nonlinear optical property was tested by using Kurtz powder method and found to have better SHG efficiency than that of potassium dihydrogen ortho phosphate (KDP).

Key words: Slow Evaporation Method; Single Crystal X-Ray Diffraction; Nonlinear Optical Materials, Inorganic Compounds

I. INTRODUCTION

The non-linear optical materials play an important role in second harmonic generation, optical communications and opto electronics. The search for new frequency conversion materials over the past decade has concentrated primarily on organic compounds [1 & 2] and many organic NLO materials with high non-linear susceptibilities have been discovered. However the implementation of single crystal, organic materials in practical device applications has been impeded by their often inadequate transparency, poor optical quality and low laser damage threshold. Hence, intense attention has been paid to inorganic materials showing the second order non-linear optical effects because of their higher non linearity [3 & 4]. Inorganic materials possess excellent mechanical, chemical and thermal properties when compared to organic crystals [5]. In the recent past, there have been extensive efforts to develop new inorganic, organic and semi-organic materials that possess several attractive properties such as high damage threshold, wide transparency range and high non-linear coefficient which make them suitable for frequency doubling [6 & 7]. KDP is the most widely used NLO material. It is characterized by good UV transmission, high damage threshold but still their NLO coefficients are relatively low. In addition they are also excellent electro – optic crystals as pocket cells, Q-switches etc. [8 – 13]. Many methods have been tried to increase the growth rate and improve the NLO properties of the KDP crystal [14 & 15]. The addition and their influence on the growth process and properties of crystals have been tried in recent years [16 & 17]. KDP and ADP are continued to be interesting materials as they exhibit excellent electro-optic and NLO properties in addition to interesting electrical properties. The demand for high quality large ADP and KDP single crystals increases due to their application as frequency conversion crystal in inertial confinement fusion [18].

In the present investigation, to enhance the quality of KDP crystals with better nonlinear optical properties an attempt has been made to grow KDP crystals from the aqueous solution added with magnesium chloride by slow evaporation method at room temperature. The grown crystals have been subjected to single crystal x-ray diffraction, FTIR, optical transmission, thermal, mechanical and NLO studies.

II. EXPERIMENTAL PROCEDURE

A. Synthesis:

Single crystals of pure KDP and magnesium chloride added KDP were grown by slow evaporation of the saturated aqueous solution at room temperature. Analytical reagent grade (AR) samples of potassium dihydrogen ortho phosphate and magnesium chloride were used for the growth of single crystals. A solution of potassium dihydrogen ortho phosphate and magnesium chloride was prepared in the ratio of 3:1. This solution was heated and left for evaporation to dryness at room temperature. The purity of synthesized salt was increased by successive recrystallization.

B. Growth Procedure:

The saturated solution of synthesized salt was taken in a beaker and the solution was filtered twice using borosil filter paper to remove the suspended impurities. The filtered solution was taken in a beaker which was tightly closed with thick filter paper so that the rate of evaporation could be minimized. After 30 days the good quality crystals were harvested (Fig.1 & 2).

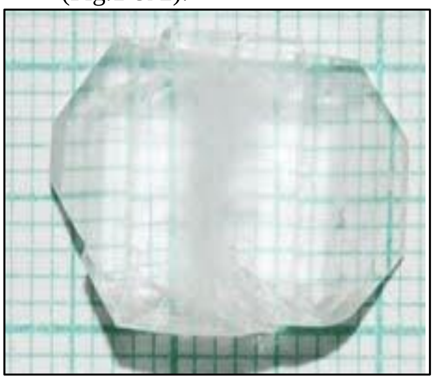

Fig. 1: Pure KDP Crystal

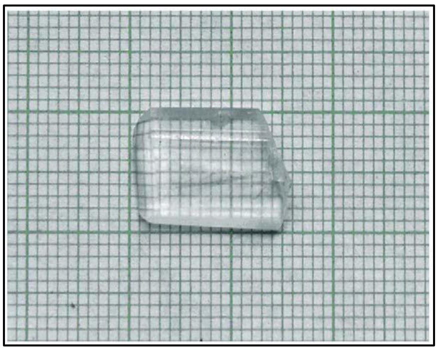

Fig. 2: Magnesium Chloride added KDP Crystal

C. *Characterization:*

The grown crystals of pure KDP and magnesium chloride added KDP were confirmed by Enraf Nonis CAD4 diffractometer. The functional groups were identified using Perkin Elmer RXI FTIR spectrometer by KBr pellet technique in the range of 400 – 4000 cm-1. The optical properties of the crystals were examined between 190 and 1100 nm using Lambda 35 UV-Vis-NIR spectrometer. The thermal behaviour of the grown crystals was tested by SDT Q600 V8.3 thermal analyzer. The Microhardness measurements of grown crystals were carried out using a Leitz Weitzler Vicker's Micro hardness tester with a diamond pyramidal indenter. The NLO property of the crystal was confirmed by Nd: YAG laser.

III. RESULTS AND DISCUSSION

A. *Single Crystal X-Ray Diffraction Analysis:*

The grown crystals were subjected to single crystal X-ray diffraction analysis to confirm the crystallinity and also to estimate the lattice parameters by employing Enraf Nonis CAD4 diffractometer. From the single crystal X-ray diffraction data, it is observed that the grown crystals are tetragonal in structure. The lattice parameters were observed for the grown crystals and tabulated in Table. 1.

Parameters	Pure KDP	Magnesium Chloride added KDP
a (Å)	7.45	7.41
b (Å)	7.45	7.41
c (Å)	6.97	6.94
Cell Volume ($Å^3$)	387	383
α (^{o})	90	90
β (^{o})	90	90
γ (^{o})	90	90
System	Tetragonal	Tetragonal

Table 1: Crystallographic Parameters of Pure and Magnesium Chloride Added KDP

B. *FTIR Spectral Analysis:*

The FTIR spectrum of the grown crystals revealed at room temperature in the range of 400 – 4000 cm^{-1} is shown in Fig.3 & 4. The O-H stretching band due to water of crystallization of KDP is observed at 3941 cm^{-1}.

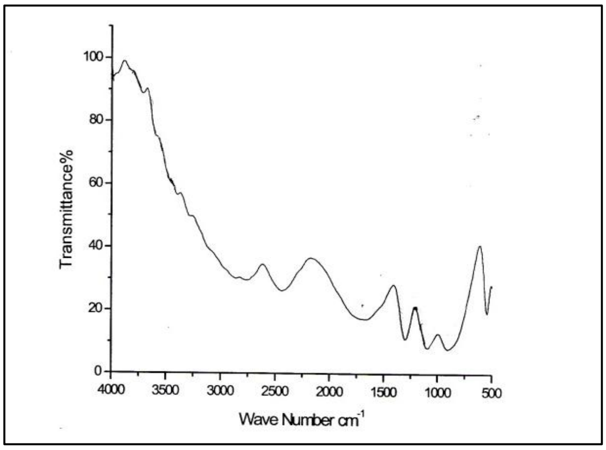

Fig. 3: FTIR Spectrum of Pure KDP Crystal

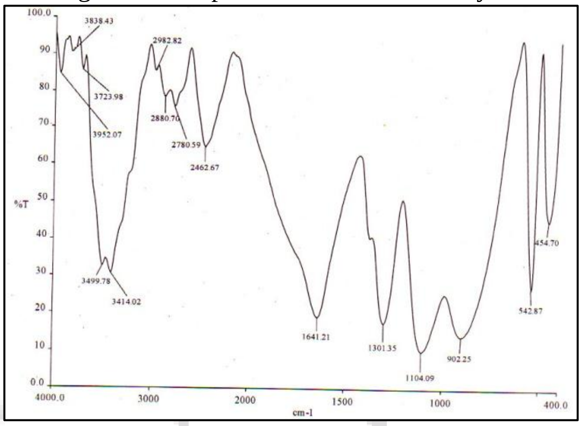

Fig. 4: FTIR Spectrum of Magnesium Chloride Added KDP Crystal

In magnesium chloride added KDP, this peak is shifted to 3952.07 cm-1. Similarly, the O-H vibrations of water due to P-OH group pf KDP are observed at 3896 and 3782 cm-1. In In magnesium chloride added KDP, these peaks are shifted are shifted 3838.43 and 3723.98 cm-1. The peak observed at 3499.78 is attributed to NH2 asymmetric stretching. The O-H stretching hydrogen bonded peak observed at 3428 cm-1 of KDP is shifted to 3414.02cm-1 in In magnesium chloride added KDP. The C-H aliphatic stretching band super imposed with NH stretching band of KDP is observed at 2924 cm-1. This is shifted to 2982 cm-1. The P-O-H symmetric and asymmetric stretching bands of KDP are attributed to 2844 and 2782 cm-1 respectively. In magnesium chloride added KDP, these peaks are shifted to 2880.70 and 2780.59 cm-1. The peaks observed at 2462.67 and 1641.27 cm-1 are attributed to O=P-OH asymmetric and symmetric bands. The peaks observed at 1301.35, 1104.09 and 902.25 cm-1 are attributed to C-N-H, P=O and P-O-H stretching bands. The peaks observed at 542.87 and 454.70 cm-1 are attributed to HO-P-OH bending and N-H torsional oscillation respectively from a comparison of the spectra with that of KDP [19]. The FTIR spectral band assignments are tabulated in Table. 2.

Wave number (cm^{-1})		Assignments
Pure KDP [19]	Magnesium Chloride added KDP	
3941	3952.07	O-H stretching due to water of crystallization
3896 3782	3838.43 3723.98	O-H vibrations of water P-OH group

---	3499.78	NH2 asymmetric stretching
3428	3414.02	O-H stretching hydrogen
2924	2982.82	bonded
		C-H aliphatic stretching
2844	2880.70	super imposed
2782	2780.59	with NH stretching
2464	2462.67	P-O-H symmetric
1642	1641.21	stretching
1300	1301.35	P-O-H asymmetric
1095	1104.09	stretching
904	902.25	O=P-OH asymmetric
542	542.87	stretching
458	454.70	O=P-OH symmetric
		stretching
		C-N-H Stretching
		P=O Stretching
		P-O-H stretching
		HO-P-OH bending
		N-H torsional oscillation

Table 2: FTIR Spectral Band Assignments of Pure and Magnesium Chloride Added KDP

C. *Optical Studies:*

The optical properties of a material are important, as they provide information on the electronic band structure, localized state and types of optical transitions. Fig.5 & 6. show the UV visible spectrum of pure KDP and magnesium chloride added KDP crystals. From the spectrum, it is observed that both the pure and magnesium chloride added KDP crystals show little absorbance in the entire visible region. The addition of magnesium chloride seems to have increased the crystalline perfection in KDP thereby resulting in lesser absorbance when compared to pure KDP. The cut off wavelength is around 210 nm for pure and added KDP crystals. The UV-Vis data reveals that magnesium chloride additive improves the optical transparency of the crystal and confirms the betterment of optical quality.

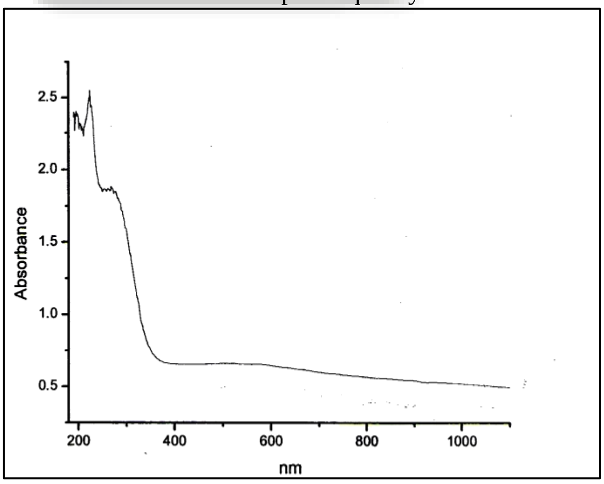

Fig. 5: UV-Vis-NIR Spectrum of Pure KDP Crystal

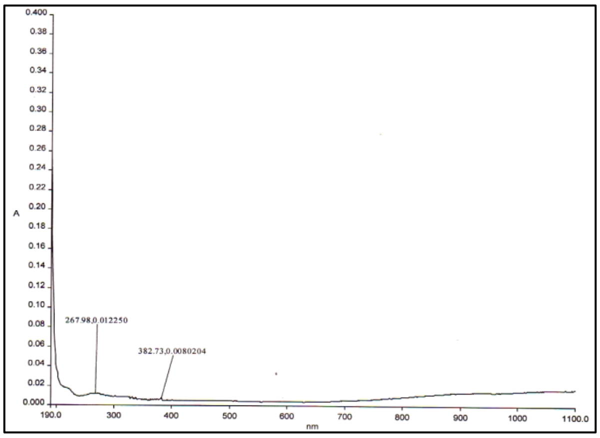

Fig. 6: UV-Vis-NIR Spectrum of Magnesium Chloride added KDP Crystal

D. *Atomic Absorption Studies:*

Atomic absorption spectroscopic (AAS) study for magnesium chloride added KDP crystal was carried to confirm the presence of magnesium chloride in the lattice of the crystal. From this study, it was observed that the concentration of magnesium chloride is 35.4 ppm. During the growth of magnesium chloride added KDP crystal, it was observed from AAS study that only low concentration of magnesium chloride has incorporated into the lattice of the magnesium chloride added KDP crystal.

E. *Thermal Studies:*

The TG/DTA analysis of the crystal was carried out in air atmosphere at heating rate of 200 C/min. The thermal analyses give information on the thermal stability, thermal decomposition and products formed on decomposition. The TG/DTA curves of pure and magnesium chloride added KDP crystals recorded in temperature range 25-700o C are shown in Fig. 7 & 8.

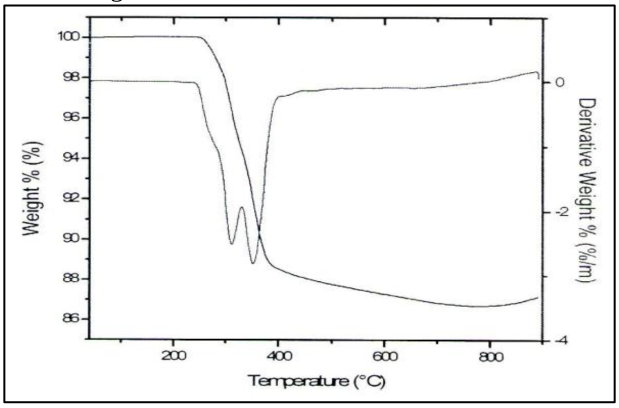

Fig. 7: TG/DTA Curve of Pure KDP Crystal

The recorded TGA curve of pure KDP exhibits negligible weight loss in the region 50 and 200o C. The decomposition of pure KDP crystal begins at 230o C and terminates at 350o C. The weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP. From the TGA curve of magnesium chloride added KDP, it is observed that the decomposition starts at about 230o C and terminates at 370o C which is possibly due to the decomposition of KDP and remaining magnesium chloride. It is observed that the crystal of pure KDP is 350o C whereas in magnesium chloride added KDP crystal the thermal stability increased 370o C. This study confirms the increase in the thermal stability of magnesium chloride added KDP crystal. Thus the thermal stability of the crystal has improved due to the presence of additive magnesium chloride.

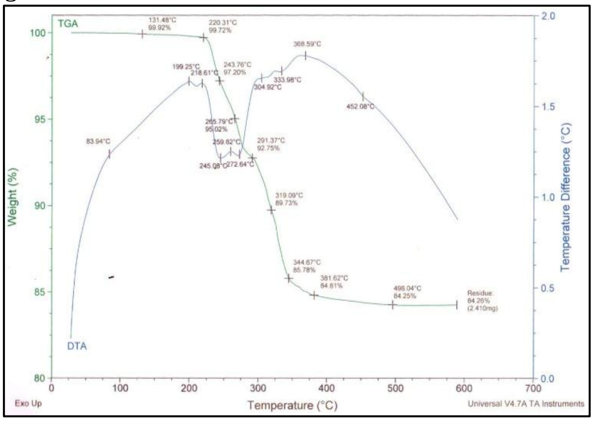

Fig. 8: Added KDP Crystal. 8. TG/DTA Curve of Magnesium Chloride

F. *Mechanical Properties:*

The hardness of the crystal carries information about the strength, molecular bindings, yield strength and elastic constants of the material. The Microhardness studies have been carried out on the KDPMC crystal using a Leitz Weitzler tester fitted with Vicker's diamond pyramidal indenter. Vicker's Microhardness values have been calculated using Hv = 1.8544 P/d^2 kg/mm^2, *P* is the applied load in kg, *d* is the average diagonal length in mm of the indentation mark. Hardness values have been taken for various applied loads over a fixed interval of time. The indentation time was kept for 5 sec. for all the loads. The graphs plotted between hardness number (Hv) and applied load (P) for pure and magnesium chloride added KDP are shown in Fig.8 & 9.

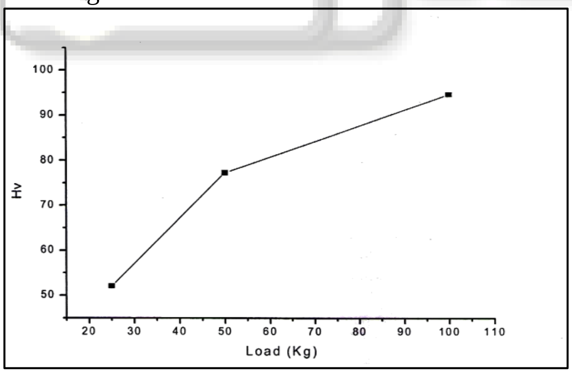

Fig. 9: Microhardness Curve of Pure KDP Crystal

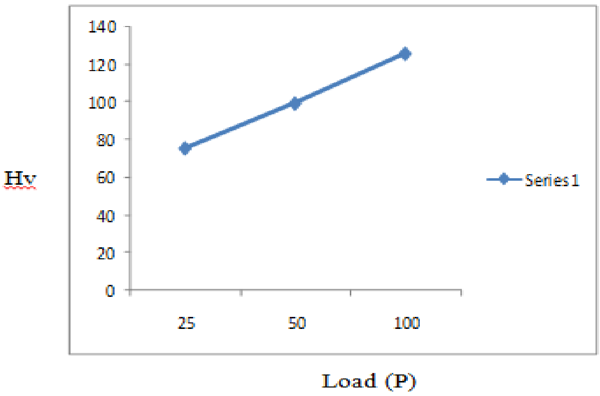

Fig. 10: Load P

From the Figure, it is observed that the hardness value of the magnesium chloride added KDP is higher than the hardness of the pure KDP crystal. The addition of magnesium chloride increases the hardness of the crystal. This is because of the incorporation of the magnesium chloride into superficial crystal lattice and removing defect centers which reduce the weak lattice stresses on the surface.

G. *Second Harmonic Generation:*

The second harmonic generation (SHG) test on the KDPMC crystal was performed by Kurtz powder SHG method [20]. The powdered sample of crystal was illuminated using the fundamental beam of 1064 nm from Q-switched Nd:YAG laser. Pulse energy 4ml/pulse and pulse width of 8 ns and repetition rate of 10Hz were used. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm collected a monochromator after separating the 1064 nm pump beam with an IR-blocking filter. A photomultiplier tube is used as a detector. It is observed that the measured SHG efficiency of KDPMC crystal was 0.5 times that of potassium dihydrogen phosphate (KDP).

IV. CONCLUSION

Optical quality and good transparency single crystals of pure and magnesium chloride added KDP were grown employing slow evaporation solution growth technique. The grown crystals have been confirmed by using single crystal X-ray diffraction studies and the lattice parameters of magnesium chloride added KDP are slightly changed due to the addition of magnesium chloride. The FTIR spectrum reveals that the functional groups of the grown crystals. The optical quality of the grown crystals was justified by UV-Vis studies. There is an increase in Vicker's Microhardness of magnesium chloride added KDP. Atomic absorption study confirms the presence of magnesium chloride in the lattice of additive KDP crystal. The TG/DTA study reveals that the presence of additive slightly increases the thermal stability of the KDP crystal. The second harmonic generation test has been confirmed by the Kurtz powder test.

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