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Spectral, Thermal and Nonlinear Optical Properties in KDP Doped Magnesium Bromide Crystals

Cicil Ignatius*

Department of Physics, Dhanalakshmi Srinivasan Engineering College, Perambalur, India

*Corresponding Author: Cicil Ignatius, Department of Physics, Dhanalakshmi Srinivasan Engineering College, Perambalur, India; E-mail: cicil1965@gmail.com

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ABSTRACT

The additive of magnesium bromide 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 bromide 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. 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).

Keywords: Slow evaporation method, Single crystal X-ray diffraction, Nonlinear optical materials, Inorganic compounds

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 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.

Inorganic materials possess excellent mechanical, chemical and thermal properties when compared to organic crystals. 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. 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. 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 bromide 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.

MATERIALS AND METHODS

Synthesis

Single crystals of pure KDP and magnesium bromide added KDP were grown by slow evaporation of the saturated aqueous solution at room temperature [1]. Analytical Reagent grade (AR) samples of potassium dihydrogen ortho

phosphate and magnesium bromide were used for the growth of single crystals. A solution of potassium dihydrogen ortho phosphate and magnesium bromide 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.

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 [2]. 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 (Figure 1).

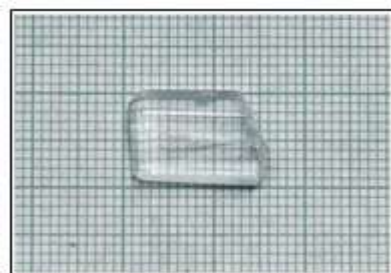


Figure 1. Grown crystal

RESULT AND DISCUSSION

Characterization

The grown crystals of pure KDP and magnesium bromide 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 cm^{-1} - 4000 cm^{-1} . The optical properties of the crystals were examined between 190 nm 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 [3]. 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.

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.

FTIR spectral analysis

The FTIR spectrum of the grown crystals revealed at room temperature in the range of 400 cm^{-1} - 4000 cm^{-1} is shown in Figures 2 and 3. The O-H stretching band due to water of crystallization of KDP is observed at 3941 cm^{-1} .

In magnesium bromide added KDP, this peak is shifted to 3952.07 cm^{-1} . Similarly, the O-H vibrations of water due to P-OH group of KDP are observed at 3896 cm^{-1} and 3782 cm^{-1} . In magnesium bromide added KDP, these peaks are shifted to 3838.43 cm^{-1} and 3723.98 cm^{-1} . The peak observed at 3499.78 cm^{-1} is attributed to NH_2 asymmetric stretching [4]. The O-H stretching hydrogen bonded peak observed at 3428 cm^{-1} of KDP is shifted to 3414.02 cm^{-1} in magnesium bromide 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} .

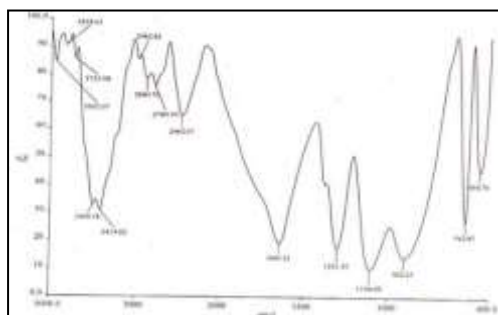


Figure 2. FTIR spectrum of KDP doped magnesium bromide

The P-O-H symmetric and asymmetric stretching bands of KDP are attributed to 2844 cm^{-1} and 2782 cm^{-1} respectively. In magnesium bromide added KDP, these peaks are shifted to 2880.70 cm^{-1} and 2780.59 cm^{-1} . The peaks observed at 2462.67 cm^{-1} and 1641.27 cm^{-1} are attributed to O=P-OH asymmetric and symmetric bands. The peaks observed at 1301.35 cm^{-1} , 1104.09 cm^{-1} and 902.25 cm^{-1} are attributed to C-N-H, P=O and P-O-H stretching bands [5]. The peaks observed at 542.87 cm^{-1} 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. The FTIR spectral band assignments.

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. Figure 3 show the UV visible spectrum of pure KDP and magnesium bromide added KDP crystals. From the spectrum, it is observed that both the pure and magnesium bromide added KDP crystals show little absorbance in the entire visible region [6]. The addition of magnesium bromide 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 bromide additive improves the optical transparency of the crystal and confirms the betterment of optical quality.

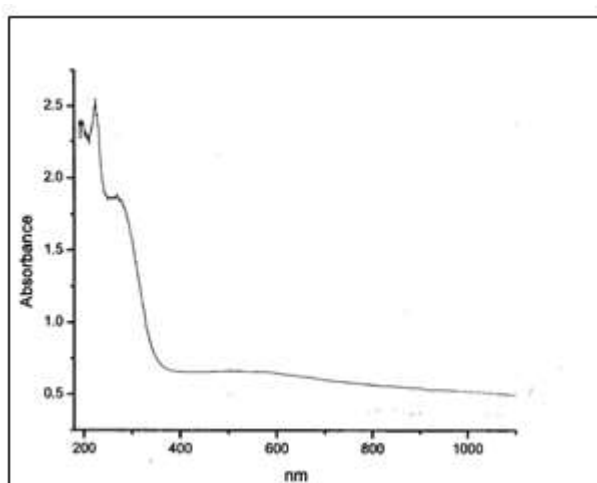


Figure 3. UV spectrum of KDP doped magnesium bromide.

Thermal studies

The TG/DTA analysis of the crystal was carried out in air atmosphere at heating rate of $20^\circ\text{C}/\text{min}$. The thermal analyses give information on the thermal stability, thermal decomposition and products formed on decomposition. The TG/DTA curves of pure and magnesium bromide added KDP crystals recorded in temperature range 25°C - 70°C are shown in Figure 4.

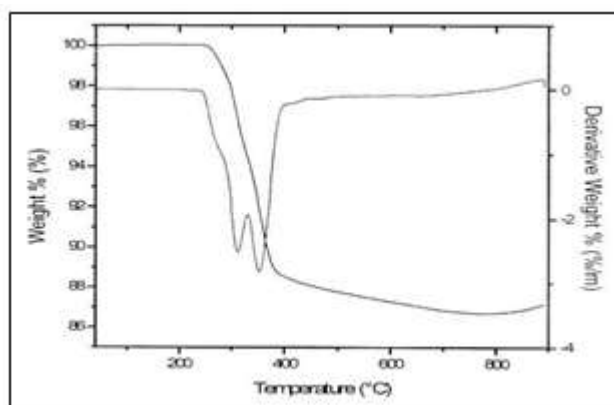


Figure 4. FRAP activity of fermented and non-fermented black and yellow soybean seed and sprout extract

The recorded TGA curve of pure KDP exhibits negligible weight loss in the region 50°C and 200°C . The decomposition of pure KDP crystal begins at 230°C and terminates at 350°C . The weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP. From the TGA curve of magnesium bromide added KDP, it is observed that the decomposition starts at about 230°C and terminates at 370°C which is possibly due to the decomposition of KDP and remaining magnesium bromide. It is observed that the crystal of pure

KDP is 350°C whereas in magnesium bromide added KDP crystal the thermal stability increased 370°C [7]. This study confirms the increase in the thermal stability of magnesium bromide added KDP crystal. Thus the thermal stability of the crystal has improved due to the presence of additive magnesium bromide.

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 KDPMB crystal using a Leitz Weitzler tester fitted with Vicker's diamond pyramidal indenter. Vicker's microhardness values have been calculated using $H_v = 1.8544 P/d^2$ kg/mm², 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 [8-10]. 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 bromide added KDP are shown in Figure 5.

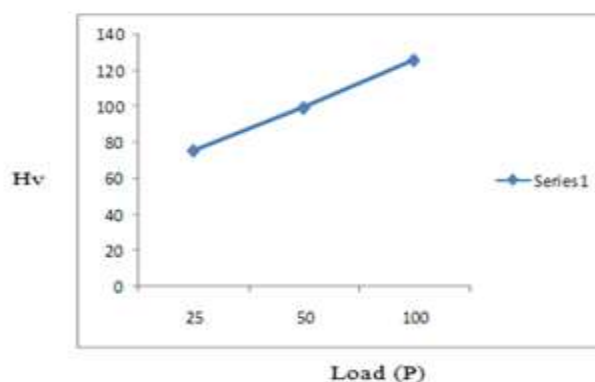


Figure 5. Microhardness curve of KDPMB crystal

From the Figure, it is observed that the hardness value of the magnesium bromide added KDP is higher than the hardness of the pure KDP crystal [11-13]. The addition of magnesium bromide increases the hardness of the crystal. This is because of the incorporation of the magnesium bromide into superficial crystal lattice and removing defect centers which reduce the weak lattice stresses on the surface.

Second harmonic generation

The Second Harmonic Generation (SHG) test on the KDPMB crystal was performed by Kurtz powder SHG method. The powdered sample of crystal was illuminated using the fundamental beam of 1064 nm from Q-switched Nd:YAG laser. Pulse energy 4 ml/pulse and pulse width of 8 ns and repetition rate of 10 Hz 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 KDPMB crystal was 0.5 times that of Potassium Dihydrogen Phosphate (KDP.)

CONCLUSION

Optical quality and good transparency single crystals of pure and magnesium bromide 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 bromide added KDP are slightly changed due to the addition of magnesium bromide. 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 bromide added KDP. Atomic absorption study confirms the presence of magnesium bromide 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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