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Effect of thiourea on the optical properties of Di-sodium hydrogen phosphate (DSHP) single crystal

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Non linear optics (NLO) materials have acquired a new significance with the advent of a large number of devices utilizing solid – state lasers sources and wide applications in the field of telecommunication, optical data storage and information devices. The Di-sodium hydrogen phosphate (DSHP) is a well known inorganic NLO material for various optoelectronics applications. In the present investigation we have grown thiourea doped Di- sodium hydrogen phosphate crystal from the aqous solution. We could enhance the SHG efficiency of thiourea doped DSHP crystal. It was **2.2** times more than pure DSHP. We observed the large enhancement in nonlinearity for high concentration of thiourea. The powder X-ray diffraction analysis confirmed the crystal structure. The incorporation of thiourea in the grown crystal was qualitatively analyzed from FT-IR study. The UV-Visible spectral study revealed that the incorporation of thiourea in DSHP enhances the transmittance of DSHP. The thermal study of grown crystal was carried out by thermogravimetric analysis.

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1. Introduction

Nonlinear optical materials are expected to be active elements for optical communication and optoelectronics. Intense attention has been paid to inorganic materials showing the second order nonlinear optical effects because of their higher nonlinearity. Among the nonlinear phenomenon, frequency doubling, frequency mixing and electro – optic modulation are important in the field of optical image storage and optical communication [1-6]. The organic additive such as thiourea has emerged a new class of promising nonlinear materials because of its superior qualities over inorganic materials [7]. The Di-sodium hydrogen phosphate (DSHP) is an interesting inorganic NLO material. M.Gunasekaran published his work on growth and characterization of Di – Sodium hydrogen phosphate [8].

The reason for choosing the thiourea as dopant is that it has well known nonlinear property [9]. Thiourea belongs to orthorhombic crystal system, its molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds, and thiourea is typical polar molecule [10].

In the present investigation, we have grown the thiourea doped DSHP crystal with improved nonlinearity. We observed high enhancement in SHG efficiency of DSHP when it was mixed with 6 mole% thiourea.

Therefore 6 mole% thiourea doped DSHP crystal was grown by slow evaporation solution growth technique. Incorporation of thiourea in DSHP was analyzed by FT-IR analysis. The optical study was carried out to observe the optical absorption. The thermal behavior of grown crystal was studied by thermogravimetric (TGA) analysis.

2. Experimental

2.1 Synthesis and growth

The Di -sodium hydrogen phosphate (DSHP) salt was dissolved in Millipore water. The purity of salt was obtained by repeated recrystallization. The solution of DSHP salt was prepared in a slightly under saturation condition. The solution was stirred well for six hours constantly using magnetic stirrer, then solution was filtered using Whatmann filter paper. The optically active organic additative thiourea was added in 2,4and 6 mole percent in different beakers of pure DSHP solution and stirred well. The pure and thiourea doped DSHP solutions were poured in different Petri dishes. We have harvested seeds of these pure and thiourea doped DSHP crystal within four to five days. The salts of 2, 4 and 6 mole percent thiourea doped DSHP were subjected to SHG test and we observed more enhancements for 6 mole percent of thiourea.

Therefore the single crystal of 6 mole % thiourea doped DSHP was grown by employing the slow evaporation technique in constant temperature bath of controlled accuracy ±0.01^{o}C at temperature 35^{o}C where the super saturation was achieved. After the period of 25 days the large size crystal of thiourea doped DSHP crystal was harvested. The photograph of grown crystal is shown in Fig. 1.

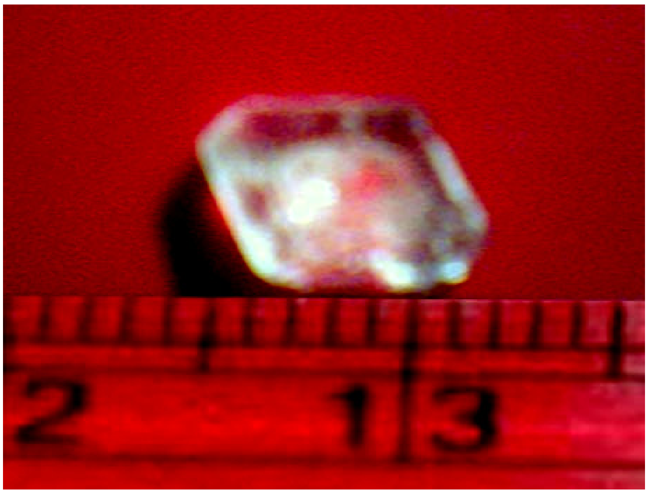


Fig. 1. 6 mole % thiourea doped DSHP crystal.

2.2 Characterization

The grown crystal was characterized by SHG efficiency test, Powder X-ray diffraction, FTIR analysis, UV-visible spectral studies and thermal analysis by thermogravimetric analysis (TGA).

3. Results and discussion

3.1 SHG efficiency

In order to confirm the enhancement of nonlinearity of DSHP due to addition of thiourea, the specimen was subjected to Kurtz powder NLO test, which employed the fundamental beam of wavelength "λ" 1064nm from Q switched Nd: YAG laser. The out put from Nd: YAG laser was used as a source and it was illuminated to the crystal specimen. The laser input of 3mJ/pulse with repetition rate of $10H_Z$ and pulse width 8ns was used. The photomultiplier tube was used as detector. The incident beam was focused by a lens of focal length 6cm. The scattered light was collected at 90°to incident beam. The second harmonic signals generated in the crystalline sample were confirmed from emission of green radiation by the sample. We have observed out put voltage of 4 mV and 9 mV for pure DSHP and 6mole% thiourea doped DSHP respectively. This indicates that the SHG efficiency of 6 mole% thiourea doped DSHP is **2.25** times more than pure DSHP. This indicates that the SHG efficiency of thiourea doped DSHP crystal is high as compare to pure DSHP. This is due to the fact that the sulfur present in thiourea is more electro negative. This causes more delocalization of electrons in case of thiourea doped DSHP crystals. This increases the non centrosymmetric structure of DSHP hence enhances its non linearity [11].

3.2 Powder X-ray diffraction

X-ray diffractometer analysis was carried out using CuKα radiation λ = 1.5406°A from a X-ray generator setting 45kV, 40mA.The Powder samples was scanned in steps of 0.02° for a time interval of 10.3377 sec over a 2θ range of 10° to 120 ° intensity. The X-ray pattern of the thiourea doped DSHP samples is as shown in Fig. 2.

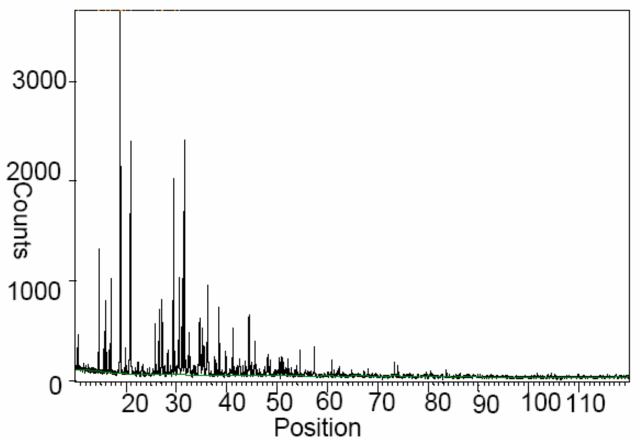


Fig. 2. Powder XRD pattern.

Table 1. Lattice parameter values of pure and thiourea doped DSHP crystals.

Sample	a (A°)	b (A°)	c (A°)	V ($A^{°3}$)
Pure DSHP	9.243	10.955	10.421	1051.8
Thiourea doped DSHP	8.204	11.018	10.442	939.44

3.3 Fourier transformation infrared spectroscopy (FTIR) analysis

The different functional groups present in the material of grown crystal were detected from Fourier transform infrared spectral study. The spectrum was recorded in the wavelength range 600 -4000cm^{-1} using Perkin Elmer FTIR spectrometer. The FTIR spectrum is shown in Fig. 3. The band at 3747cm^{-1} may be due to the incorporation of added NH_2 group of thiourea [12]. The intense peak at 3442 cm^{-1} corresponds to P(O)-OH bond. The peak at 2985.65 cm^{-1} is due to γ_1 vibration belonging to a_2 irreducible representation [13]. The peak observed at 863.76 cm^{-1} may be attributed to γ_3 vibration of a_1 representation. The γ_7 vibration of e irreducible representation is observed 550.96 cm^{-1} .There is slightly changed in the vibrational frequency of different functional groups of DSHP due to addition thiourea [8].

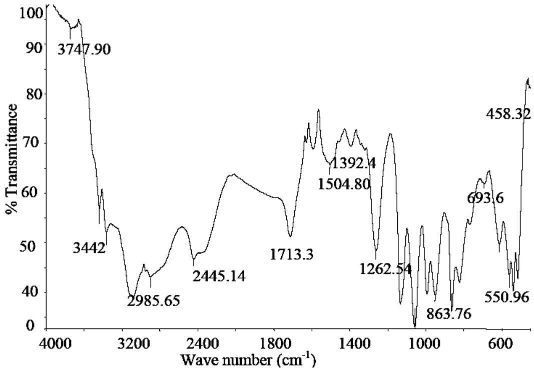
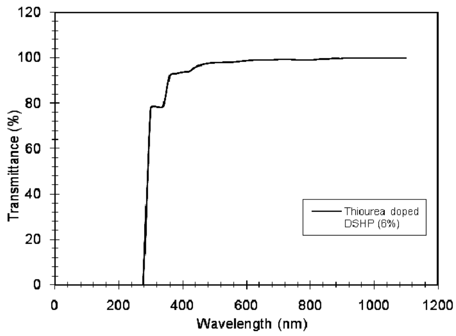


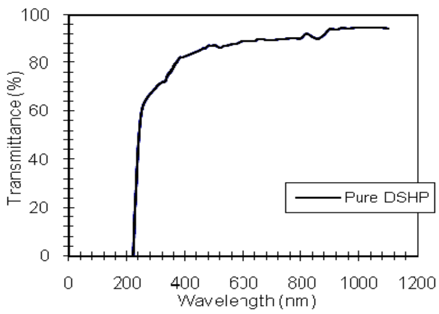
Fig. 3. FTIR spectrum of thiourea doped DSHP crystal.

3.4 UV-Visible spectral study

The transmission spectrum plays a vital role in identifying the potential of a NLO material because a given NLO material can be utility only if it has a wide transparency widow without any absorption at the fundamental and second harmonic wave lengths preferably with the lower limit of the transparency window being well below the 300 nm limit [14]. The UV-visible spectral studies of grown thiourea doped DSHP crystals were carried out using Perkin Elmer spectrophotometer. The transmission spectrum was recorded in the wavelength region from 200 to 1200 nm and spectrums of thiourea doped DSHP and pure and DSHP crystal are shown in



(a)



(b)

Fig. 4 (a). Transmittance spectrum of thiiourea doped DSHP crystal ; (b). Transmittance spectra of pure DSHP crystal.

Fig. 4 (a, b). The spectra showing the 100% transmittance in the thiourea doped DSHP crystal. It may be due the more electro negativity of thiourea in comparison of the sodium. Thus the thiourea doped DSHP crystal can be used as better alternative to pure DSHP in optoelectronics applications.

3.5 Thermogravimetric analysis (TGA)

Thermo gram provides information about decomposition pattern of materials and weight loss [15]. The thermo gravimetric methods are limited to decomposition and oxidation reaction. Thermogravimetric analysis of grown thiourea doped DSHP crystal was carried out using TAQ-500 thermo gravimetric analyzer between temperature limit -50°C to 800°C at a heating rate of 25°C/min in a nitrogen inert atmosphere. The resulting thermogram is shown in Fig. 5. There is weight loss of about 50% between the temperature ranges 50°C to 100° it may due to loss of water of crystallization and weakly adsorbed one. There is minute loss occurred with the maximum between the temperature limit from 100 to 300°C. The resulting residue is found to be thermally stable without any decomposition.

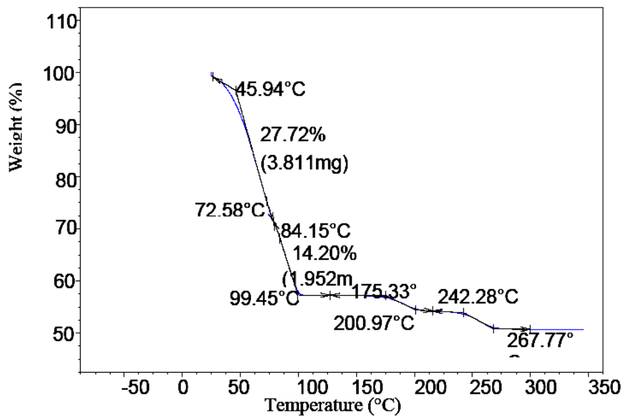


Fig. 5. TGA thermogram of thiourea doped DSHP crystal.

4. Conclusions

The single crystal of thiourea doped DSHP crystal was grown by slow evaporation solution growth method.

1. The powder XRD confirms its crystal structure.
2. The incorporation of thiourea in DSHP was confirmed by FT-IR Study. The spectra revealed that due to addition of thiourea the frequency vibration of different functional group are slightly shifted.
3. The good optical transparency shows the possible application of the material in the field of NLO.
4. The SHG test shows that the optically active carbon in thiourea reacts with hydrogen of DSHP and enhanced the non Centro symmetric structure of host and hence its nonlinearity increases.

5. The thermogravimetric analysis revealed that thiourea doped DSHP crystal is thermally less stable than pure DSHP.

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