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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.11, pp 4601-4607, Oct-Nov 2014

# Synthesis And Characterisation Of Cadmium Sulphate Doped L - Threonine Dihydrogen Phosphate Crystal

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**Abstract:** Cadmium sulphate doped L- Threonine dihydrogen phosphate crystals have been successfully grown by slow evaporation method. X-ray diffraction studies were used to determine the cell parameters. The structural and optical properties of the grown crystals were analyzed by FT-IR and UV-vis-NIR spectral studies. The dielectric property of grown crystals was established by dielectric measurements. Vickers microhardness test was also carried out to elucidate the mechanical behavior of the grown crystals. FESEM – EDAX and ICP-OES studies confirm the presence of phosphorous and cadmium sulphate in the crystal. The second harmonic generation (SHG) behavior of the grown crystal was confirmed by Kurtz-Perry powder technique.
**Keywords**: FTIR spectral study, UV–vis–NIR study, Dielectric study, Micro hardness, SHG.

## Introduction

Amino acid based compounds are, in general, capable of producing second harmonic generation. This will be more useful in the fabrication of optoelectronic and photonic devices. In the recent years, efforts have been made on organic-metal mixed amino acid crystals in order to improve the chemical stability, laser damage threshold and nonlinear optical properties. Several researchers have carried out a lot of studies on pure and metal ions-doped aminoacid crystals [1-4]. Hence, new nonlinear optical materials are needed for photonic applications and other device fabrications in optoelectronics.

Aminoacid material L-Threonine dihydrogen phosphate (LTDP) has been reported as a promising NLO material with SHG efficiency higher than that of KDP [5]. A new material can be synthesized by doping LTDP with Cadmium sulphate to analyze the change in the NlO activity of the material. In the present study, Cadmium sulphate doped LTDP crystal has been successfully grown by slow evaporation technique. Characterization studies such as single crystal XRD, FT-IR, UV-vis-NIR, FESEM – EDAX and ICP-OES analyses, and dielectric, Vickers micro hardness studies have been carried out for the grown crystal. The second harmonic generation efficiency of the grown crystal has been finally determined by Kurtz-Perry powder technique.

### 1. Growth of cadmium sulphate doped LTDP crystal

Crystals of LTDP doped with cadmium sulphate were grown from the aqueous solution of L-Threonine (Loba) and ortho-phosphoric acid in 1:2 molar ratio mixed with 2 mol % cadmium sulphate by slow evaporation method. The aqueous solution was stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temp. The solution gradually achieved supersaturation due to slow evaporation for the onset of growth process. After a period of 30 days, transparent crystals with dimensions $12x3x2mm^3$ were harvested. Figure 1 shows the photograph of as - grown cadmium sulphate doped LTDP crystal.

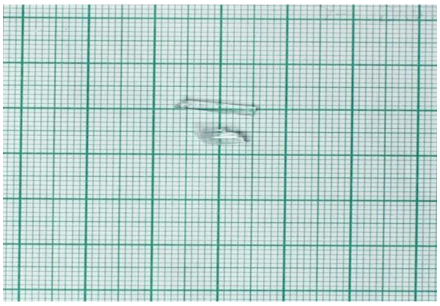

**Figure1: Photograph of the as - grown cadmium sulphate doped LTDP crystal**

## 2.Single crystal X-ray diffraction study

Single crystal X-ray diffraction study of the grown crystal was carried out using ENRAF NONIUS CAD - 4 X-ray diffractometer. XRD analysis has confirmed that the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. The space group suggests that the grown material is noncentrosymmetric which fulfils the fundamental criterion for the material to exhibit NLO behavior. The lattice parameters of the LTDP and cadmium sulphate doped LTDP crystals are shown in Table1 for comparison. The variations in the cell parameters and the crystal system show the incorporation of cadmium sulphate in LTDP crystal.

**Table 1: Lattice parameters of LTDP and $CdSO_4$ doped LTDP**

| **Lattice parameter** | **LTDP** | **$CdSO_4$ doped - LTDP** |
|---|---|---|
| a (Å) | 5.140 | 5.160 |
| b (Å) | 7.720 | 7.760 |
| c (Å) | 13.580 | 13.680 |
| Crystal System | Monoclinic | orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ |
| Volume($Å^3$) | 540.00 | 547.00 |

## 3. FT-IR Spectroscopic Analysis

FT-IR spectrum was recorded for the sample in the range 450 - 4000 $cm^{-1}$ using the instrument FT-IR 4100 type spectrometer. The functional groups were assigned from the FTIR spectrum (Figure 2) as follows. The peaks at 3172, 1417 $cm^{-1}$ indicate the presence of carboxylic acid group corresponding to O-H stretching vibrations. The peak at 2047cm-$^{1}$ shows N=C= S stretching vibrations. The peaks at 1346 cm-$^{1}$ confirm the presence of sulphate. The peak due to 1318, 1479 $cm^{-1}$ are due to Nitro groups. The peaks due to 1183,1247,1109,931 $cm^{-1}$ confirm the presence phosphate in the crystal. The peak at 1040 $cm^{-1}$ corresponds to amine group C-N stretching vibration. The bending vibrations of CH stretch are found corresponding to the peaks at 907,871,665,622 cm-$^{1}$. The peaks due to 701,739,769,804 , $cm^{-1}$ reveal the presence of alkene group. Table 2 presents the various functional groups present in the grown material cadmium sulphate doped LTDP.

**Table 2: Functional groups of cadmium sulphate doped LTDP crystal**

| **Wavenumber ( $cm^{-1}$ )** | **Spectroscopic Assignments** |
|---|---|
| 3172,1417 | carboxylic acid group O-H stretch |
| 2047 | N=C=S stretch |
| 1626 | N-H bending vibrations |
| 1346 | sulphate group |
| 1318,1479 | nitro groups |
| 1183,1247,1109,931 | phosphate group |
| 1040 | C-N stretch amine group |
| 907,871,665,622 | C-H stretching |
| 701,739,769,804 | alkene group |

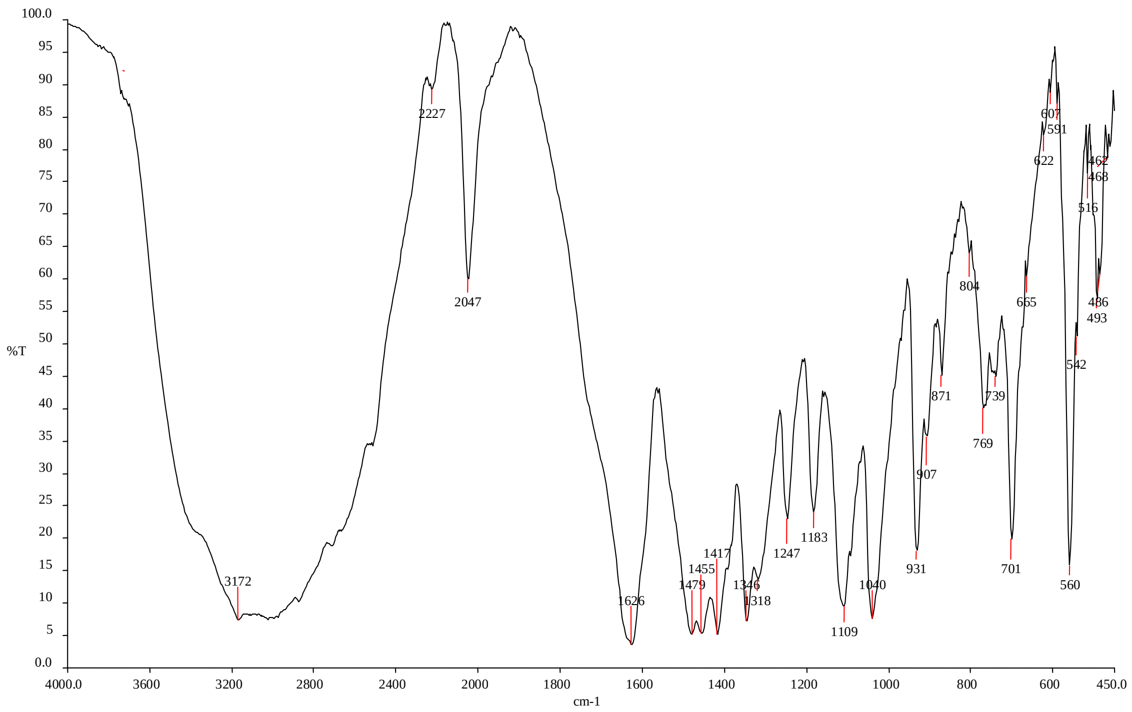


**Figure 2: FT-IR spectrum of cadmium sulphate doped LTDP crystal**

### 4.UV-vis-NIR Studies

For optical device fabrications, the grown crystal should be highly transparent over a wide range of wavelength. The optical transmission spectrum recorded in the range 190 -1100 nm is shown in Fig.3. From the spectrum, it is observed that the transmission of the crystal is considerably high in the wavelength region 190-1100 nm. The UV cut off wavelength for the grown crystal is found to be 235 nm which makes it a potential material for optical device fabrications.

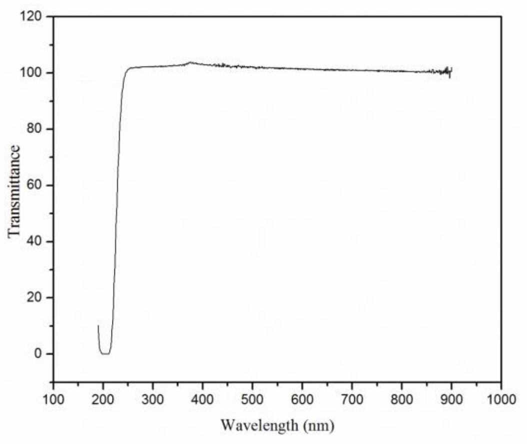


**Figure 3 :UV– vis- NIR transmission Spectrum of cadmium sulphate doped LTDP crystal**

### 5.Dielectric Studies

The dielectric behavior of cadmium sulphate doped LTDP crystal was studied using HIOKI 3532 LCR HITESTER. The sample of dimensions 8.30x2.03x1.42 $mm^3$ has been placed inside a dielectric cell whose capacitance was measured at temperature (40°C) for different frequencies from 50Hz to 5MHz. The dielectric constant (ε) and dielectric loss(ε') have been calculated using the formulae $\varepsilon = c\, d / A\, \varepsilon_0$ and $\varepsilon' = \varepsilon D$ where d is the thickness of the sample, A is the area of the sample, $\varepsilon_0$ is permittivity of free space and D is the dissipation factor. The dielectric constant of the grown crystal as a function of frequency is shown in Fig.4. From the graph, it is seen that the dielectric constant decreases with increase in frequency. The large value of dielectric constant at low frequency is due to the contribution by all the polarizations, namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significant polarizations gradually. The dielectric loss was studied as a function of frequency and it has been shown in Fig.5.The lower values of dielectric loss at higher frequencies suggest that the crystal contains minimum density of defects.

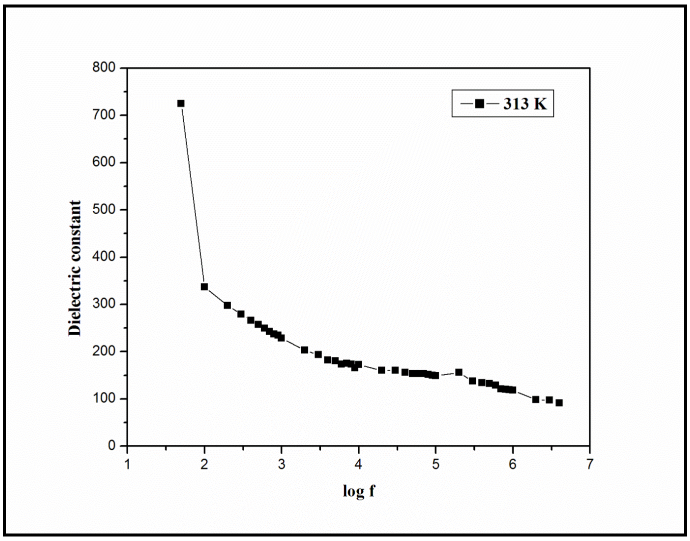


**Figure 4 Plot of dielectric constant Vs log f for cadmium sulphate doped LTDP crystal**

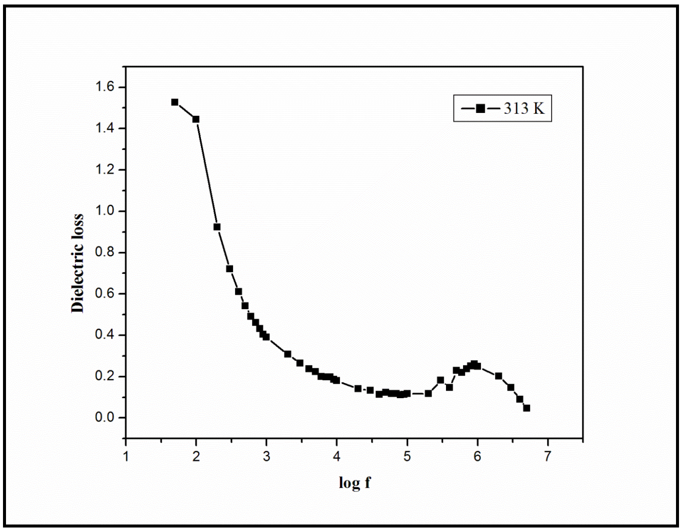


**Figure 5 Plot of dielectric loss Vs logf for cadmium sulphate doped LTDP crystal**

## 6.Vickers microhardness test

The fastest and simplest method to evaluate the mechanical properties of the crystal is the hardness measurement. Cadmium sulphate doped LTDP crystals which are transparent and free from cracks, were selected for microhardness measurements. Micro hardness studies were carried out for the cadmium sulphate doped LTDP using Leitz Wetzler Vickers microhardness tester by varying the applied load from 25g to 100g. The indentation time was kept at 5s for all the loads. Fig.6 shows the variation of Vickers hardness number with applied load P for (010) plane of the cadmium sulphate doped LTDP crystal. It is observed that the hardness number increases with the increases of load. The value of work hardening coefficient (n) of the cadmium sulphate doped LTDP crystals was determined as 2.2 from the slope (Fig.7) of the plot of logP vs logd. According to Onitsch, if n is less than 3, the hardness number will increase with increase in load [6]. The hardness number is found to be increasing with the doping concentration of cadmium sulphate in the lattice of LTDP doped with cadmium sulphate confirming the prediction of onitch[7].

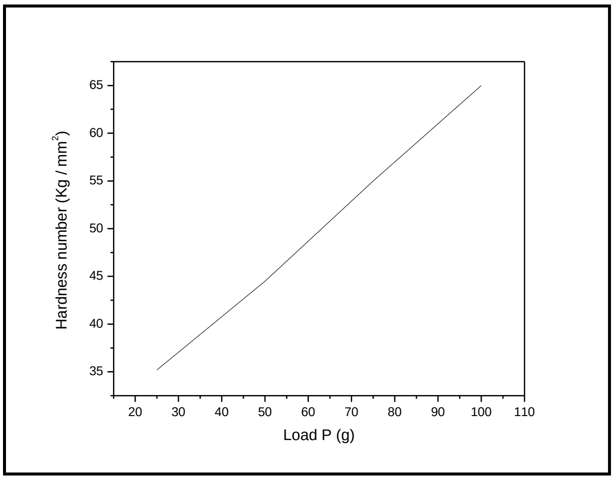


**Figure 6: Plot of hardness number vs load P**

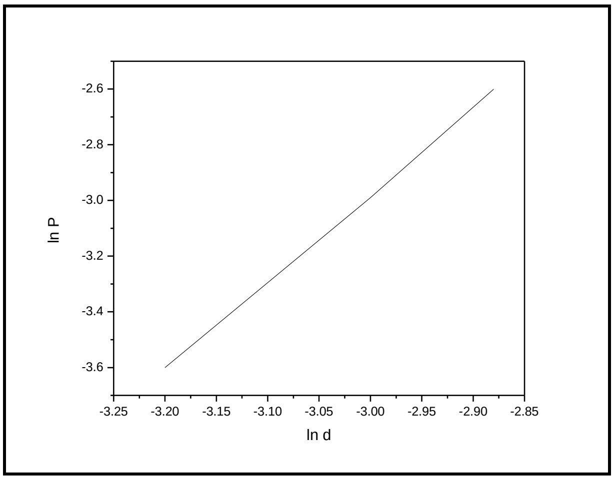


**Figure 7 : Plot of ln P vs ln d**

## 7. EDAX and ICP-OES Analyses

The grown crystal was analyzed by INCA200 energy dispersive X-ray micro analyzer equipped with LED steroscon 440 scanning electron microscope. Fig.8 shows the EDAX spectrum of cadmium sulphate doped LTDP crystal which confirms the presence of elements phosphorous, carbon, nitrogen, oxygen, sulphur and cadmium in the grown crystal. Table 3 presents the compositional analysis of zinc sulphate doped LTDP crystal. The crystal was then subjected to inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis using Perkin Elmer optima 5300 DV Spectrometer. The crystal was crushed into pieces and grounded using an agate mortar. The powder sample weighing 100 mg was transferred to 200 ml flask with the help of funnel for analysis. The result of ICP-OES analysis shows the characteristic wavelengths 213.617 and 228.802 nm which confirm the presence of phosphorus and cadmium with concentration of 58.39 and 8.158 mg per litre [8] .

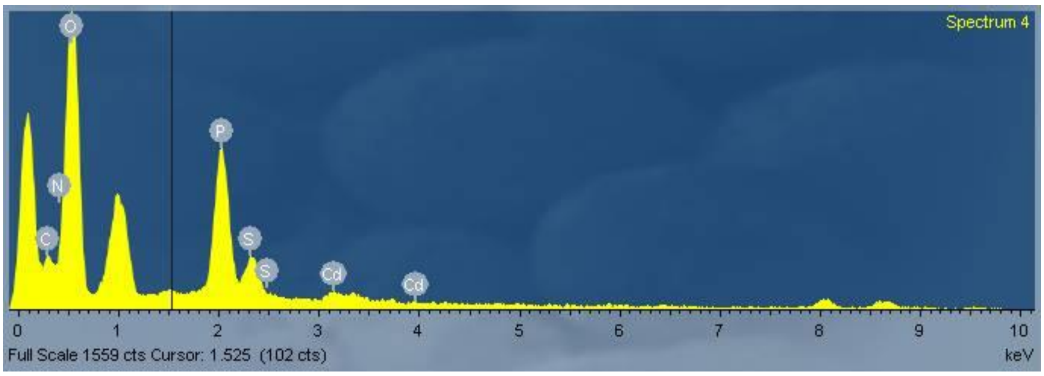

**Figure 8 : EDAX spectrum cadmium sulphate doped LTDP crystal**

**Table 3: Compositional analysis of $CdSO_4$ doped LTDP from EDAX Analysis**

| Element | Weight % | At % |
|---|---|---|
| C K | 6.70 | 9.61 |
| N K | 9.15 | 11.26 |
| P K | 12.49 | 6.95 |
| O K | 64.73 | 69.74 |
| Cd L | 3.35 | 0.51 |
| Total | 100.00 | |

## 8. FESEM analysis

FESEM analysis was carried out in order to study surface features of the grown crystals. Fig.9 shows the microstructural image of cadmium sulphate doped LTDP crystal with resolution 50.0um. The surface feature reveals the smooth and transparent nature of the surface with different components present in the grown crystal.

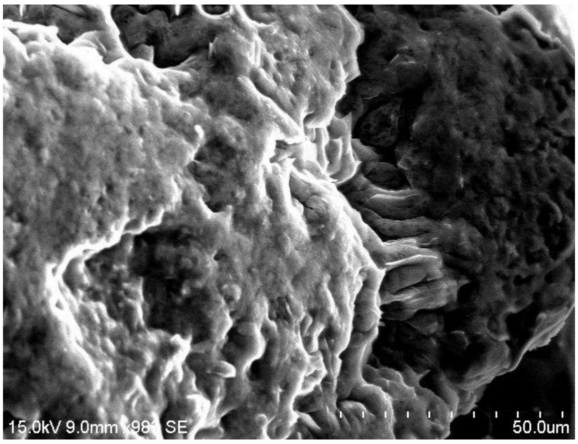


**Figure 9 : FESEM Images of cadmium sulphate doped LTDP crystal**

## 9.NLO studies: Second harmonic generation efficiency

Kurtz powder SHG technique was extremely useful for the initial testing of the materials for second harmonic generation [9]. The sample was illuminated using Q-switched mode locked Nd: YAG laser with the fundamental beam of wavelength 1064 nm and input pulse 0.68J. The emission of green radiation in the crystal confirmed the second harmonic signal generation in the crystal. The output power (17.8 mJ) of the sample was measured and compared with that of (8.9mJ) reference material KDP. The SHG efficiency of LTDP crystal is thus found to be twice that of KDP. Hence, cadmium sulphate doped L- threonine dihydrogen phosphate crystal is one of the excellent material to find wide applications in optoelectronic and photonic devices.

## 10.Conclusion

Cadmium sulphate doped LTDP crystals were grown by slow evaporation technique. From single crystal XRD analysis it is confirmed that the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. FESEM-EDAX and ICP-OES analysis confirm the presence of phosphate and cadmium sulphate in the crystal. From UV- vis- NIR spectrum, the transmission range was calculated. FTIR analysis confirms the presence of functional groups present in the grown crystal. The dielectric property of grown crystals was established by dielectric measurements. Mechanical behavior has been studied by Vickers microhardness test.

Kurtz - Perry powder technique confirms that cadmium sulphate doped LTDP is one of the promising nonlinear optical materials with SHG efficiency twice that of KDP. Therefore, cadmium sulphate doped LTDP crystal can be used in photonic and optoelectronic industries due to improved optical properties.

**Acknowledgements**

The author wishes to thank SAIF IIT Madras, Loyola College, Crescent Engg College and NCNSNT (University of Madras) for their kind support and help to complete this work

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