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Growth and Characterisation of Zinc Sulphate doped L-Threonine dihydrogen phosphate Single Crystal

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Abstract: Single crystals of Zinc sulphate doped L-Threonine dihydrogen phosphate (LTDP) have been successfully grown by slow evaporation method. The grown crystals were subjected to single crystal X-ray diffraction studies 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 studies were carried out to understand the dielectric behavior of the material. FESEM-EDAX and ICP-OES studies confirm the presence of phosphate, zinc sulphate in the crystal. The second harmonic generation (SHG) of the grown crystals was tested using Kurtz-Perry powder technique.
Keywords: Slow evaporation method, FTIR spectral study, UV- vis- NIR spectral study, Dielectric study, SHG.

1. Introduction

Non-linear optical materials have wide applications in various fields like optical data storage, photorefractive phenomenon, frequency multipliers, fibreoptics, optical switches, etc. Nonlinear optics has been a rapidly growing field in recent decades. It is based on the study of effects and phenomenon related to the interaction of intense coherent light radiation with matter. For the last several years, scientists are working on nonlinear optical (NLO) materials which combine the high optical nonlinearity and chemical flexibility of organics with the high mechanical strength of inorganics [1-3]. Hence, new nonlinear optical material are needed for photonic applications and other device fabrications in optoelectronics.

Amino acid compound L-Threonine dihydrogen phosphate (LTDP) has been reported as a promising NLO material with SHG efficiency higher than that of KDP, and can be used for the fabrication of optoelectronic devices [4]. In the present study, the title compound L-Threonine dihydrogen phosphate (LTDP) doped with zinc sulphate was successfully grown by slow evaporation technique. Characterization studies such as single crystal XRD, FT-IR, UV-vis-NIR and dielectric studies and FESEM-EDAX and ICP-OES analyses have been carried out for the grown crystal. NLO property and second harmonic generation efficiency of the grown crystal have also been analyzed by Kurtz-Perry powder technique.

2. Growth of LTDP doped zinc sulphate crystal

Single crystals of LTDP doped zinc sulphate were grown from the aqueous solution of L-Threonine and orthophosparic acid with 1: 2 molar ratio mixed with 2 mol % zinc sulphate. 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. After a period of 32 days, transparent crystals with dimensions 17x2x2 mm^3 were harvested. Figure 1 shows the photograph of as - grown zinc sulphate doped LTDP crystal.

3. 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 grown 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 requirement for the material to exhibit NLO behavior. The lattice parameters of the pure and doped LTDP crystals are shown in Table 1. The variations in the cell parameters and the crystal system confirm the incorporation of zinc sulphate in L- Threonine dihydrogen phosphate.

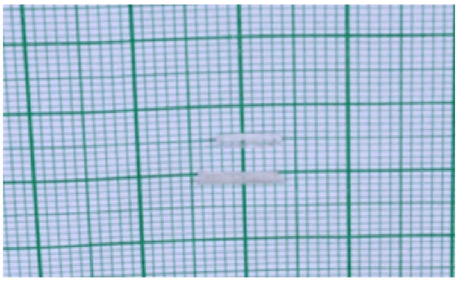

Figure 1: Photograph of the as- grown zinc sulphate doped LTDP crystal

Table 1: Lattice parameters of LTDP and $ZnSO_4$ doped LTDP

Lattice parameter	LTDP	$ZnSO_4$ doped- LTDP
a (Å)	5.140	5.200
b(Å)	7.720	7.800
c(Å)	13.580	13.710
Crystal System	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
Volume($Å^3$)	540.00	555.00

4. FT-IR Spectroscopic Analysis

The Fourier transform infrared spectrum was recorded for the sample in the range 450 cm^{-1} to 4000 cm^{-1} using the instrument FT-IR 4100 type A spectrometer. The functional groups are assigned from the FTIR spectrum (Figure 2) as follows. The peak at 3422, 3306 cm^{-1} indicates the presence of amide group, with N-H stretching vibrations. The bending vibrations of CH stretch are found corresponding to the peaks at 3057, 3031, 2970 cm^{-1}. The peak due to 2927 cm^{-1} reveals the presence of alkane group. The peaks at 2226, 1605, 1557, 1496, 1454 cm^{-1} are due to Nitro bond stretching. The peak at 1705 cm^{-1} is due to C=O stretching of carboxlicacid group. The peak at 1605 cm^{-1} correspond to conjugated C=C stretch. The peak at 1557 cm^{-1} is due to in plane bending N-H stretching. The peaks at 1410, 1337, 1299 cm^{-1} correspond to C-H bending vibration. The peaks at 10174, 1143, 1044, 1017, 1017, cm^{-1} confirm the presence of phosphate group in the crystal. The peaks at 953,893,845,799,740 cm^{-1} confirm the presence of sulphate group. Table 2 presents the various functional groups present in the grown material.

Table 2: Functional groups of zinc sulphate doped LTDP crystal

Wavenumber (cm^{-1})	**Spectroscopic Assignments**
3422, 3306	amide N-H stretch
3057, 3031, 2970	alkenes = CH stretch
2927,	alkenes
2226, 1605, 1557, 1496, 1454	nitriles- C,N triple bond Stretch
1705	carboxylic acid C=O stretch
1605	alkenes C=C Stretch conjucated
1557	amide plane N-H bend
1410, 1337, 1299	C-H bend Plane bend
1174, 1143	phosphine oxides P = O
1078	phosphines P – H Stretch
1017, 1044	phosphines P-H bend
953, 893, 845, 799, 740	sulfonates S-O stretch
702	alkenes C-H bend dissubstituted
663, 702, 663, 548, 532	alkyl halides

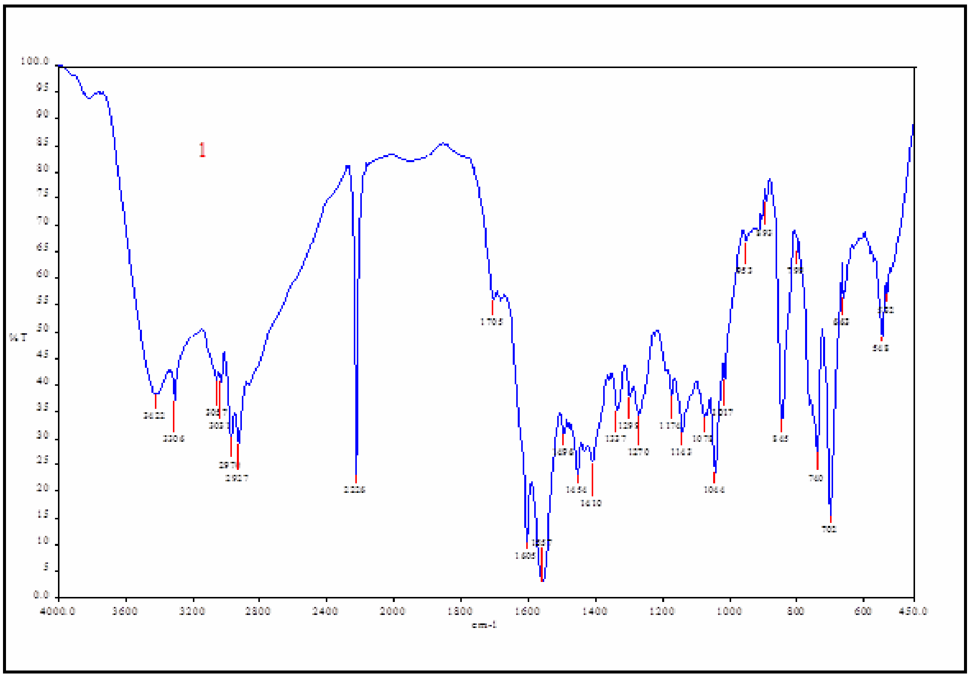

Figure 2: FTIR spectrum of zinc sulphate doped LTDP crystal

5. 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 248 nm which makes it a potential material for optical device fabrications.

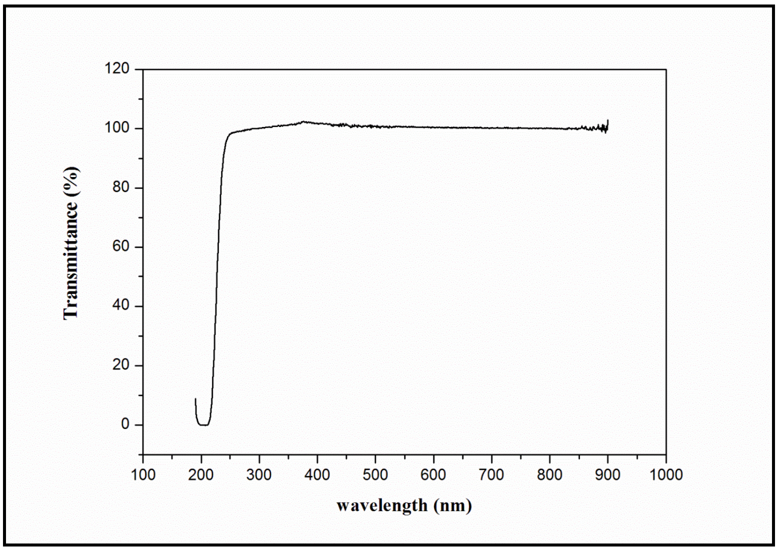

Figure 3: UV– vis – NIR transmission Spectrum of zinc sulphate doped LTDP crystal

6. Dielectric Studies

The dielectric behavior of LTDP crystal was studied using HIOKI 3532 LCR HITESTER. The experiment was carried out for the frequencies from 50Hz to 5MHz at room temp. 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 presence of 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.

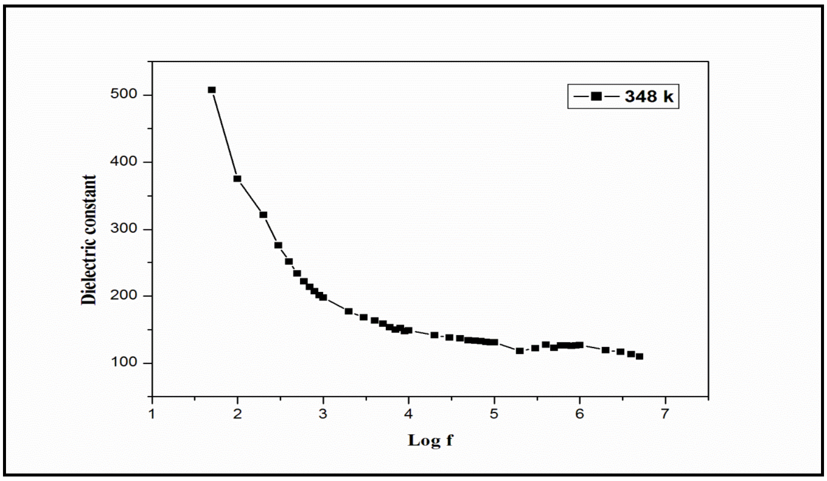

Figure 4: Plot of dielectric constant Vs logf

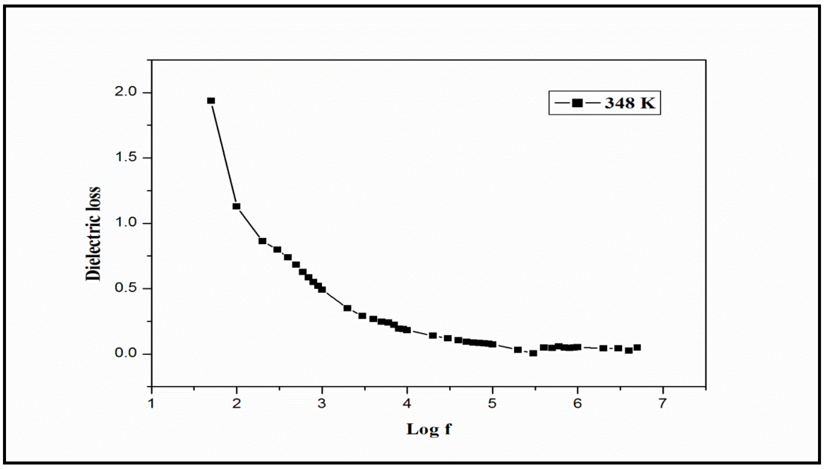

Figure 5: Plot of dielectric loss Vs logf

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.6 shows the EDAX spectrum of doped LTDP crystal which confirms the presence of elements phosphorous, carbon, nitrogen, oxygen, sulphur and zinc 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 200ml flask with the help of funnel for analysis. The results of ICP- OES analysis show the characteristic wavelengths 213.617 nm and 206.200 nm which confirm the presence of dihydrogen phosphate and zinc sulphate with concentrations of 56.38 mg and 27.99 mg per liter respectively.

Table 3: Compositional analysis of $ZnSO_4$ doped LTDP from EDAX Analysis

Element	Weight %	At %
C	36.56	42.93
N	28.13	28.33
O	30.22	26.65
P	4.01	1.83
S	0.14	0.06
Zn	0.93	0.2

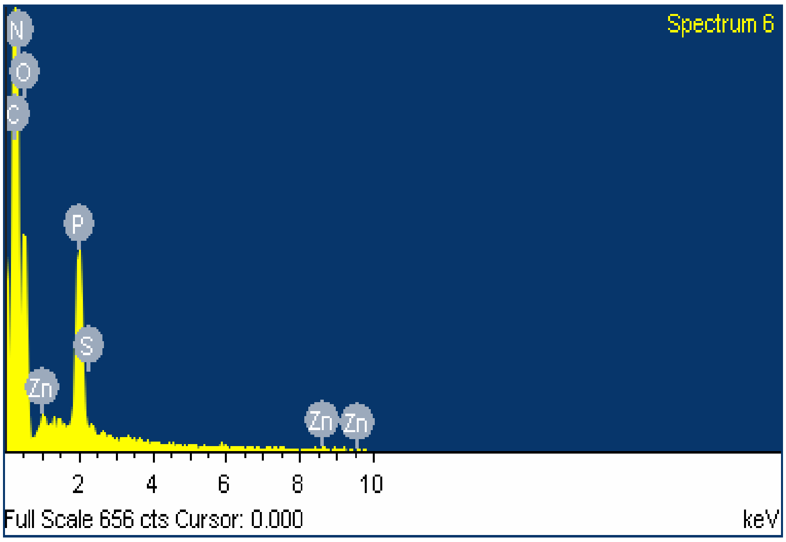

Figure 6: EDAX Spectrum of zinc sulphate doped LTDP

8. FESEM analysis

FESEM analysis was carried out in order to study surface features of the grown crystals. Fig.7 shows the microstructural image of zinc sulphate doped LTDP crystal with resolution 20.0um. The surface feature reveals the smooth and transparent nature of the surface with different components present in the grown crystal.

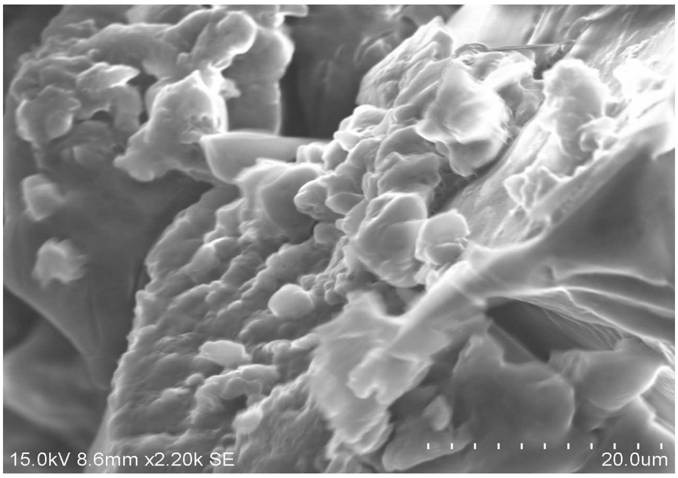

Figure 7: FESEM image of zinc sulphate doped LTDP

9. NLO studies: Second harmonic generation efficiency

Kurtz powder SHG technique was extremely useful to test second harmonic generation [5]. 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 of the sample was measured as 16.3mJ and compared with that of (8.9mJ) reference material KDP. The SHG efficiency of LTDP crystal is thus found to be 1.74 times higher than that of KDP.

10. Conclusion

Single crystals of zinc sulphate doped LTDP were grown by slow evaporation technique. From single crystal XRD analysis, it is confirmed that the crystal belongs to orthorhombic crystal system. ICP-OES and FESEM - EDAX spectral data confirmed the presence of phosphate and zinc sulphate in the grown 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 dielectrics property of grown crystals was established by dielectric measurements. Kurtz - Perry powder technique confirmed that LTDP doped zinc sulphate is one of the promising nonlinear optical material with SHG efficiency 1.74 times higher than that of KDP. Therefore, zinc sulphate doped LTDP crystal can be used in photonic and optoelectronic industries due to improved optical properties.

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