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Synthesis and characterization of magnesium chloride doped l -threonine dihydrogen phosphate crystal

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ABSTRACT

Magnesium chloride 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. Photoconductivity and dielectric studies were carried out to understand the response of the material to the incident radiation and dielectric behavior of the material. FESEM - EDAX and ICP-OES studies confirm the presence of phosphorous and magnesium in the crystal. The second harmonic generation (SHG) behavior of the grown crystal was confirmed by Kurtz-Perry powder technique.

Keywords: Slow evaporation method, FTIR spectral study, UV–vis–NIR study, photoconductivity, 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 magnesium chloride to analyze the change in the NlO activity of the material. In the present study, magnesium chloride doped LTDP crystal has been successfully grown by slow evaporation technique. Characterization studies such as single crystal XRD, FT-IR, UV-vis-NIR, FESEM with EDAX and ICP-OES analyses, photoconductivity and dielectric 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.

Materials and methods - Growth of magnesium chloride doped LTDP crystal

Crystals of LTDP doped with magnesium chloride were grown from the aqueous solution of L-Threonine (Loba) and ortho-phosphoric acid in 1:2 molar ratio mixed with 2 mol % magnesium chloride 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 35 days, transparent crystals with dimensions 16x2x2mm^3 were harvested. Figure 1 shows the photograph of as - grown magnesium chloride doped LTDP crystal.

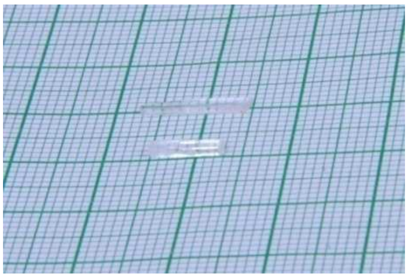

Figure1 Photograph of the as- grown magnesium chloride doped LTDP crystal

RESULTS AND DISCUSSION

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 magnesium chloride doped LTDP crystals are shown in Table1 for composition. The variations in the cell parameters and the crystal system show the incorporation of magnesium chloride in LTDP crystal

Table 1 Lattice parameters of LTDP and Magnesium chloride doped LTDP

Lattice parameter	LTDP	Magnesium chloride doped - LTDP
a (Å)	5.140	5.160
b (Å)	7.720	7.740
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	548.00

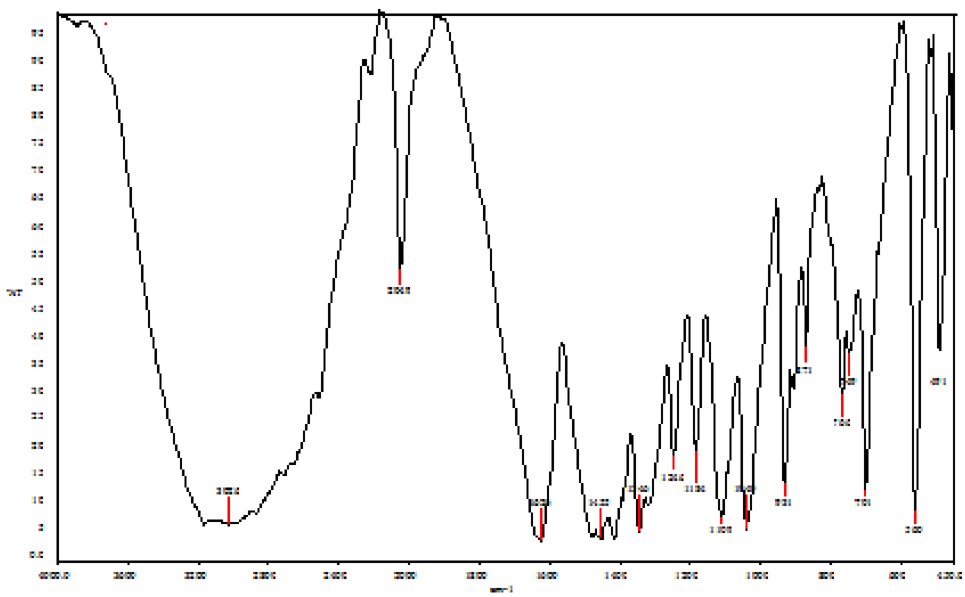

Figure 2 FT-IR spectrum of magnesium chloride doped LTDP crystal

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 peak at 3026cm^{-1}, which indicates the presence of alkenes group, corresponds to = C-H stretching vibrations. The peak at 2049 cm^{-1} reveals N=C=S stretching vibrations. The peak due to 1455 cm^{-1} corresponds to – CH_2 bending vibration alkenes group. The peak corresponding to 1346 cm^{-1} identifies CH_3 bending vibrations of alkenes group. The peaks due to 1246, 1109 cm^{-1} correspond to C-C (O)-C- stretching vibrations. The peak at 1184 cm^{-1} belongs to CF stretching vibration. The peak at 1040 cm^{-1} confirms the presence phosphate in the crystal. The peak at 931 cm^{-1} is due to C-O stretching anhydrides. The peak at 871 cm^{-1} is due to aromatic group of C-H bend (meta). The peaks against 766,749 cm^{-1} corresponds to aromatic group of C-H bend (mono). The peak due to 701 cm^{-1} identifies C-H bend dissubstituted alkene group. Table 2 presents the various functional groups present in the grown material magnesium chloride doped LTDP.

Table 2 Functional groups of magnesium chloride doped LTDP crystal

Wavenumber (cm^{-1})	Spectroscopic Assignments
3026	= CH stretch –alkenes
2049	Isothiocyanates N=C=S stretch
1626	alkenes C=C stretch isolated
1455	alkenes CH_2 bend
1346	alkenes CH_3 bend
1246,1109,	esters C-C(O)-C stretch
1184	C-F stretching
1040	phosphine oxides P=O stretch
931	anhydrides C-O stretch
871, 766,749.00	aromatic C-H bend(meta) aromatic C-H bend (mono)
701	alkenesC-H bend disubstituted
491	C-I stretching

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

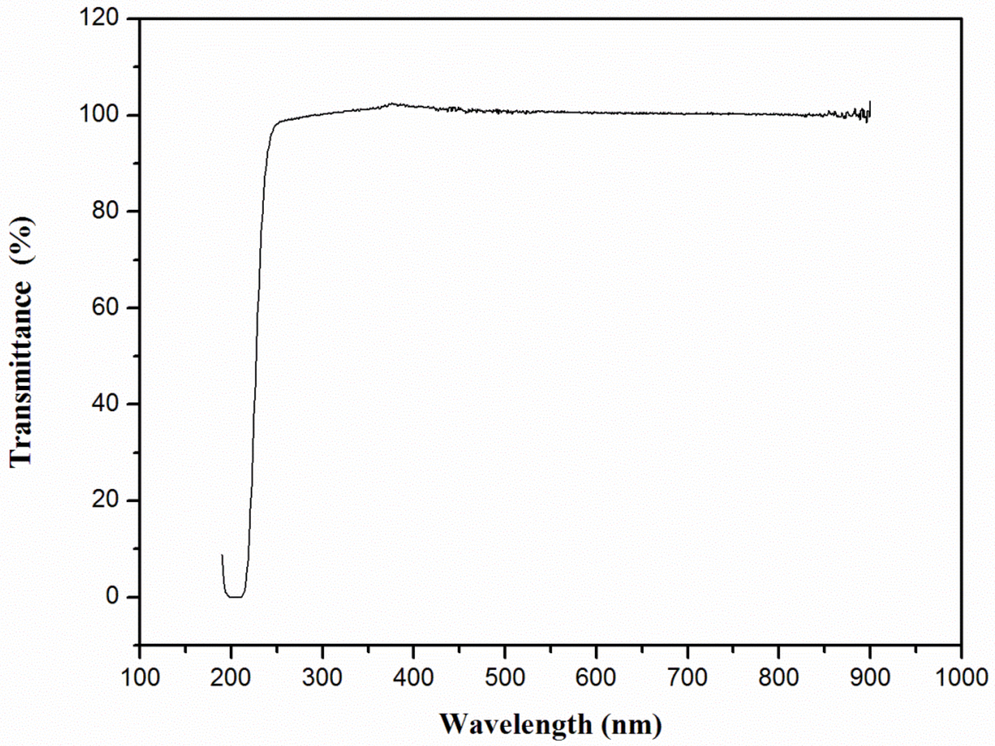

Figure 3 UV– vis- NIR transmission Spectrum of magnesium chloride doped LTDP crystal

Photoconductivity Studies

photoconductivity measurements were made using Keithly 485 picoammeter. The applied electric field was changed from 2 V / cm to 14 V / cm without exposing the sample to any radiation and the corresponding dark current was recorded. The sample was then illuminated with a halogen lamp of 100 W power and the resulting photocurrent was measured by varying the applied field in the same range as used in the case of measurement of dark current. Fig4. shows the plots of dark current (I_d) and photo current (I_p) against the applied field. It is seen from the plots that both I_d and I_p of the sample increase linearly with the applied field. It is observed from the plot that the dark current is always higher than photocurrent. The phenomenon of negative photoconductivity is explained by stockman model [5]. The negative photo conductivity in a solid is due to the decrease in the number of charge carriers (or) their life time, in the presence of radiation [6]. For negative photo conductor, forbidden gap holds two energy levels of which one is placed between the Fermi level and conduction band and the other is located close to the valance band. The second state has higher capture cross-section for electrons and holes. As it captures electron from the conduction band, the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation. Even though the material shows negative photoconductivity in the visible region, the material is capable of inducing electric polarization when the incident radiation is more intense for NLO activity.

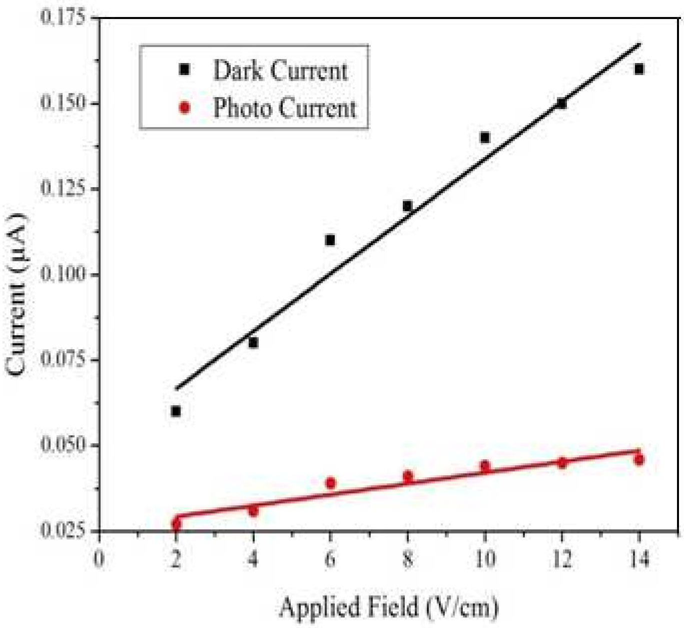

Figure 4 Photoconductivity of magnesium chloride doped LTDP crystal

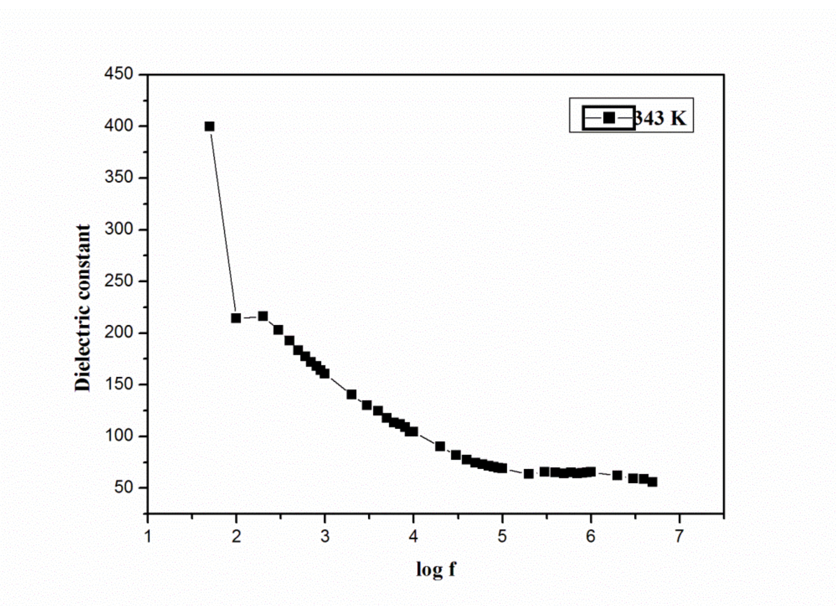

Figure 5 Plot of dielectric constant Vs log f for magnesium chloride doped LTDP crystal

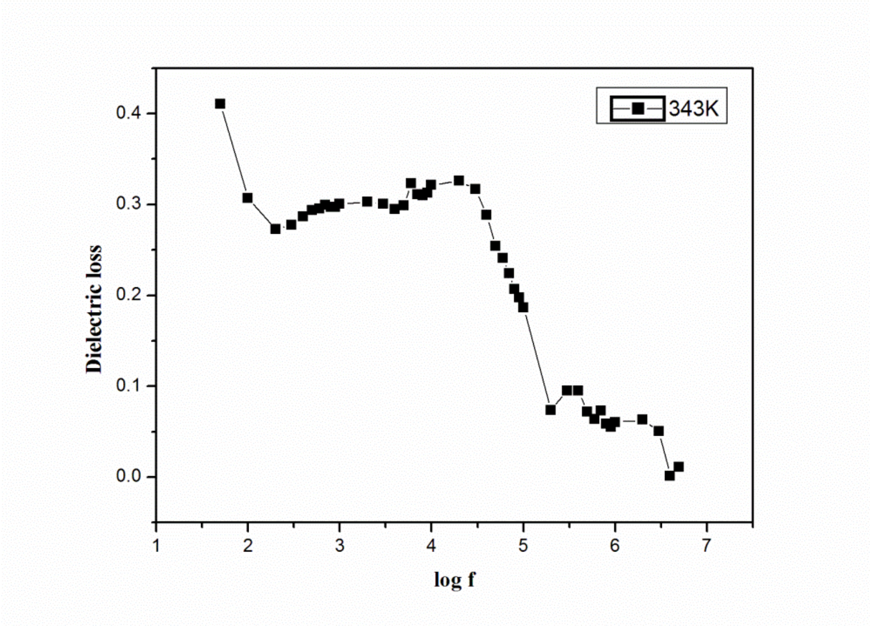

Figure 6 Plot of dielectric loss Vs logf for magnesium chloride doped LTDP crystal

Dielectric Studies

The dielectric behavior of magnesium chloride doped LTDP crystal was studied using HIOKI 3532 LCR HITESTER. The sample of dimensions 9.12x2.16x1.3 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, ε_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.5. 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.6.The lower values of dielectric loss at higher frequencies suggest that the crystal contains minimum density of defects.

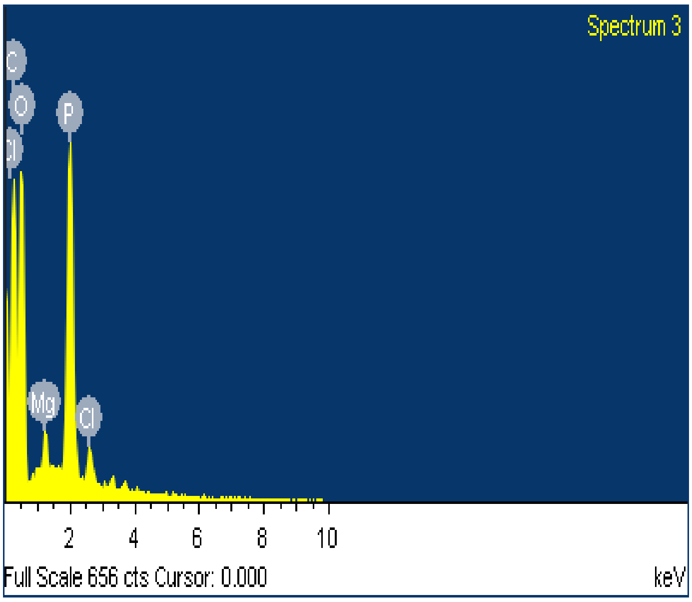

Figure 7 EDAX Spectrum of doped LTDP magnesium chloride

EDAX- 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.7 shows the EDAX spectrum of LTDP crystal which confirms the presence of phosphorus along with carbon, magnesium, oxygen and chloride in the grown crystal. Table 3 presents the compositions of magnesium chloride 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 100mg 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 285.213 nm which confirm the presence of phosphorus and magnesium with concentration of 58.39 mg and 5.617 mg per litre.

Table 3 Compositions of magnesium chloride doped LTDP crystal from EDAX analysis

Element	Weight %	Atomic %
C	46.54	56.77
O	40.46	37.05
Mg	0.96	0.58
P	10.59	5.01
Cl	1.46	0.6
Totals	100	

FESEM Analysis

FESEM analysis was carried out in order to study the surface features of the grown crystals. Fig8.shows the micro structural image of magnesium chloride doped LTDP crystal with resolution 20 um. The surface features observed in the grown crystal reveal the smooth surface with different components present in the crystal.

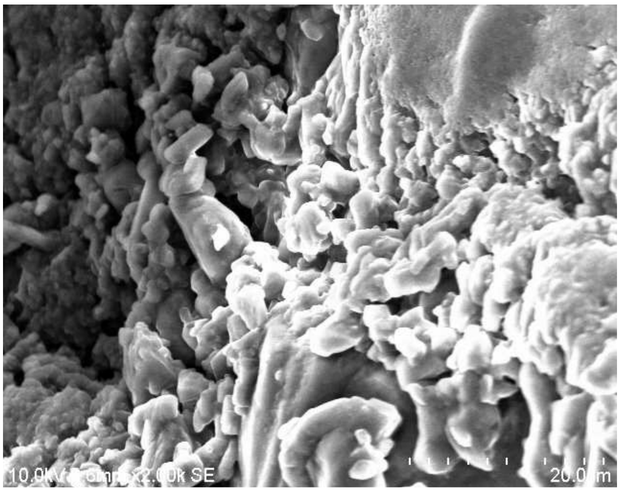

Fig 8 FESEM images for magnesium chloride doped LTDP crystal

NLO studies: Second harmonic generation efficiency

Kurtz powder SHG technique was extremely useful for the initial testing of the materials for second harmonic generation [8]. 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 16.7mJ and compared with that of (8.9mJ) reference material KDP. The SHG efficiency of LTDP crystal is thus found to be 1.78 times higher than that of KDP.

CONCLUSION

Magnesium chloride 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 $P2_12_12_1$. ICP-OES and EDAX - FESEM spectral data confirm the presence of phosphate and magnesium chloride 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. Photoconductivity investigations reveal the negative photoconductivity of the grown crystal for visible light. Kurtz - Perry powder technique confirms that magnesium chloride doped LTDP is one of the promising nonlinear optical materials with appreciable SHG efficiency of 1.78 times higher than that of KDP. Therefore, magnesium chloride doped LTDP crystal can be used in photonic and optoelectronic industries due to improved optical properties.

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