NON LINEAR OPTICAL PROPERTIES OF A DYE DOPED L-THREONINE SINGLE CRYSTALS

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ABSTRACT

Pure L Threonine and Methyl Violet doped L Threonine single crystals were grown by slow evaporation technique. The grown crystals were characterized using PXRD, UV-Visible, FTIR and NLO spectroscopies. PXRD data were collected and indexed. Grain size, microstrain and dislocation density were calculated. FTIR data provides the functional group of all the grown crystals. UV-Visible absorption spectra were recorded and the optical bandgap energy and the refractive index of the grown crystals were also determined. Grown crystals grown are violet in colour, transparent and needle shaped. They belong to the face centered orthorhombic crystal system. The optical band gap energies of all the grown crystals are almost constant. UV-Visible spectrum shows the full absorption and transmission in the entire visible region. So, the pure and Methyl Violet doped L Threonine crystals are very good material for optoelectronic applications. NLO study shows that due to the presence of the dopant dye, L Threonine has lost its SHG efficiency. Hence it can be used as semiconductors, superconductors, photonic crystals etc.

Key words: [UV –Visible, Tauc plot, band gap energy, and SHG efficiency]

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MOLECULARFORMULA

$C_4H_9NO_3$ - L Threonine

$C_{24}H_{28}N_3Cl$ - Methyl Violet

I. INTRODUCTION

Non linear optics (NLO) is the branch of optics that describes the behavior of light in nonlinear media, that is, media in which the polarization density P responds non-linearly to the electric field E of the light.

Non linear optical (NLO) materials play a major role in nonlinear optics and in particular, they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of non linear optics. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials presenting large non-linearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. Optical switching and memory by NLO effects, which depends on light intensity, are expected to result in the realization of pivotal optical devices in optical fibre communication (OFC) and optical computing which make the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed.

The NLO materials are of organic, inorganic, organic metallic (semi-organic) and polymeric material forms. The inorganic NLO materials have good mechanical strength, thermal stability and higher laser threshold damage. Some important inorganic NLO materials are ADP, KDP and KTP. The recent search is concentrated on semi-organic NLO materials have large non linearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [1 - 2]. Some organic NLO crystals grown now a days are L-Threonine, L-Alanine, L-Histadine, L-Arganine, L-Leucine, L-Valaniam, L-Lysine, L-Proline and L-Aspirin [3].

AMINOACIDS

Organic salts based on coloumbic interactions between charged molecules often show non-centro symmetric packing eg, amino acids. Non linear alpha amino acids show special features of interest such as molecular chirality and wide transparency in the visible and uv regions. All these favourable properties paved the way for the discovery of amino acid crystals such as L-Alanine, L-Threonine and semi organic compounds like L-Argininetetra fluoroborate (LAFB) etc. Amino acids are interesting materials for NLO application as they contain a protondonar carboxyl acid (-COO) group and the proton acceptor amino (NH2) group in the mandal so they exhibit molecular chirality, absence of strongly conjugated bonds and zwitterionic nature of molecule. Most amino acids are moderately water soluble and less soluble in organic solvents [4].

The amino acid crystals are used in photonic based fabrications and they show high damage threshold, wide transparency region and nonlinear optical character which make them suitable for device fabrication [5-8].

L-THREONINE

In the present investigation, pure and doped L-Threonine single crystals were grown because L-Threonine is technically and biologically important crystal. It is a small chiral naturally occurring polar amino acid which shows higher SHG efficiency than other amino acids [9-10]. Among amino acid crystals, L-Threonine is a polar uncharged class and the interaction between polar and nonpolar molecules is the fundamental concept for understanding biological properties [11-14]. The interesting physical properties of L-Threonine are high non linearity, high laser damage threshold and low refractive indices [15-16]. The optical properties displays some specific features such as wide transparency range in the visible and uv spectral region and favours crystal hardness. These properties are useful for applications in the field of telecommunications, optical information storing devices and potential material in laser system. The biological importance of L-Threonine crystals are that it helps to maintain proper protein balance in the body [17]. Some of the general properties of L-Threonine is given in the Table 1[18-19].

METHYLVIOLET

Methyl violet is a family of organic compounds that are mainly used as dyes. Depending on the number of attached methyl groups, the colour of the dye can be altered. Its main use is as a purple dye for textiles and to give deep violet colour in paint and ink, it is also used asa hydration indicator for silica gel. Methyl violet 10B is also known as crystal violet and has medical uses [20].

The term methyl violet encompasses three compounds that differ in the number of methyl groups attached to the amino functional group. They are all soluble in water, ethanol, diethylene glycol and dipropyleneglycol.

II. EXPERIMENTAL DETAILS

In the present work Methyl Violet doped L Threonine crystals are grown to enhance the optical and mechanical property of the L Threonine. Pure and Methyl Violet doped L Threonine crystals in the dopant ratio 0.002, 0.004, 0.006, 0.008 and 0.010 were grown from the aqueous solution by slow evaporation technique. The grown crystals were characterized for X-Ray Diffraction, optical property, SHG efficiency etc.

III. RESULTS AND DISCUSSION

1. X-RAY DIFFRACTION

The lattice parameters of acrystalline substance can be determined using techniques such as X-ray diffraction [21].

Grain Size:

Grain is either a single crystalline or poly crystalline material and is present either in bulk or thin film form. During the process, smaller crystalline come to closer and grow to become larger due to kinetics, most likely scenario, the grain is larger than a crystallite [22-25].

$$p = \frac{1}{D^2}$$

$$Grain\ Size, D_p = \frac{0.9\lambda}{\beta cos\theta}$$

λ - wavelength of X- ray used, $\lambda = 1.5406 \times 10^{-10}$ nm

θ-Bragg's angle of diffraction.

β- Full Width Half Maximum

D_p- crystalline size

Microstrain:

The XRD method is used to analyse structure, parameter such as microstrain, it is known that the line broadening is the result of small crystal size in the growth direction of coating, strain, stacking faults, dislocations and point defects. Microstrain is calculated using the formula,

$$\varepsilon = \frac{\beta COS\theta}{4}$$

where, β-full width at half maximum in radian, θ-Bragg's angle of diffraction.

Dislocation Density:

Dislocation density is a measure of number of dislocations in a unit volume of a crystalline material. Because the presence of dislocation strongly influence many of the properties of the materials. Dislocation density,

where, D is the grain size.

The photograph of the given crystals are shown in figure 1and 2. It can be observed that the given crystals are transparent and needle shaped.

Fig.1: Photograph of pure grown crystals

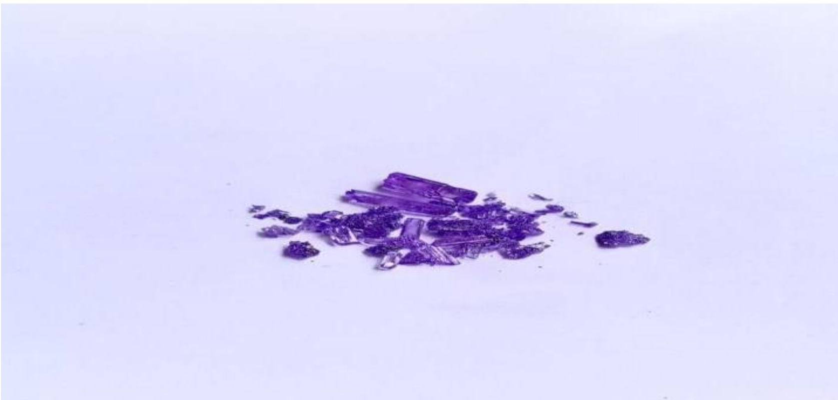

Fig. 2. 0.008% Methyl Violet doped L Threonine crystal

The X-ray diffraction pattern for the doped sample is shown in fig.3.

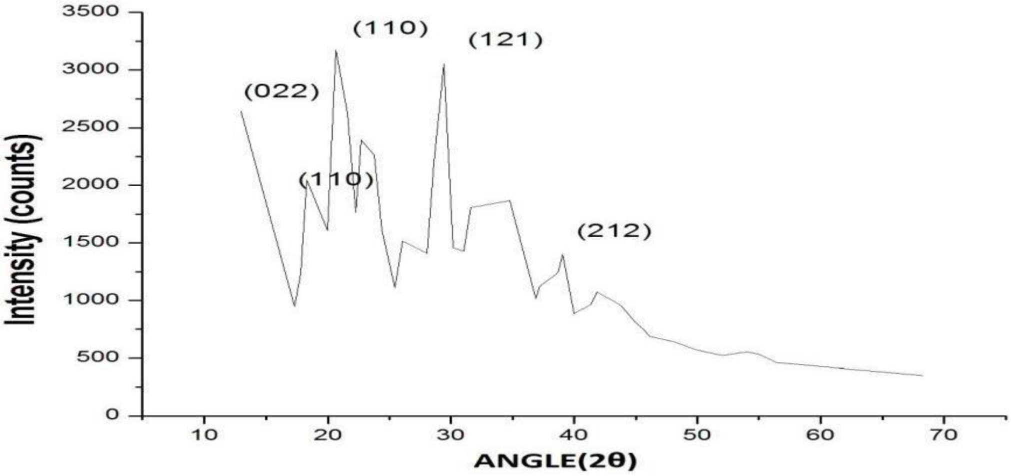

Fig .3 XRD pattern of 0.002% Methyl Violet doped L Threonine

Lattice parameters:

Lattice parameters calculated for all the grown crystals are given in the table 1. The PXRD data shows that the L Threonine single crystal belongs to Orthorhombic system with space group $P2_12_12_1$ with cell parameter values a=5.1784Å, b= 7.7184Å, c = 13.4473 Å and V = 537.4746 Å^3. The lattice parameter determined in the present investigation agreed with the literature value [21].

Table1. Lattice parameters for all the grown crystals.

System	Lattice Parameters			Volume Å^3
	a Å	b Å	C Å	
PureL-Threonine	**5.1784** **[5.19]**	**7.7184** **[7.7334]**	**13.4473** **[13.5971]**	**537.4746** **[540.4382]** **[29]**
0.002% Methyl violet doped L-Threonine	**5.1743**	**7.7288**	**13.6420**	**545.5589**
0.004% Methyl violet doped L-Threonine	**5.3224**	**7.8314**	**14.5095**	**604.0062**
0.006% Methyl violet doped L-Threonine	**5.2342**	**7.7492**	**13.5457**	**549.4252**
0.008% Methyl violet doped L-Threonine	**5.4073**	**7.7228**	**12.7256**	**531.4146**
0.010% Methyl violet doped L-Threonine	**5.2631**	**7.7582**	**13.2453**	**540.8345**

Table.2 Grain size, Micro strain and Dislocation density.

SL. NO	SYSTEM	GRAINSIZE	MICRO STRAIN	DISLOCATION DENSITY
		$\times10^{-8}$nm	$\times10^{-4}$nm	$\times10^{14}$ mho/m
1	**Pure L-Threoninecrystal**	**8.9883**	**5.4387**	**5.2416**
2	**0.002% of Methyl violet doped L-Threonine crystal**	**9.9239**	**3.5953**	**1.1057**
3	**0.004%of Methyl violet doped L-Threonine crystal**	**9.4012**	**4.8302**	**2.9667**
4	**0.006%of Methyl violet doped L-Threonine crystal**	**9.9144**	**4.2978**	**3.9798**
5	**0.008%of Methyl violet doped L-Threonine crystal**	**10.1890**	**3.7783**	**1.5065**
6	**0.01%of Methyl violet doped L-Threonine crystal**	**9.7119**	**4.2495**	**2.1930**

2. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR microscopy ideal for sample ID, multilayer film characterization, and particle analysis. It measures intensity over a narrow range of wavelengths at a time [26]. The FTIR spectrum are taken for all the grown crystals to study the spectroscopic properties. The wave numbers corresponding to the peaks and its assigned functional groups are shown in the table 3.

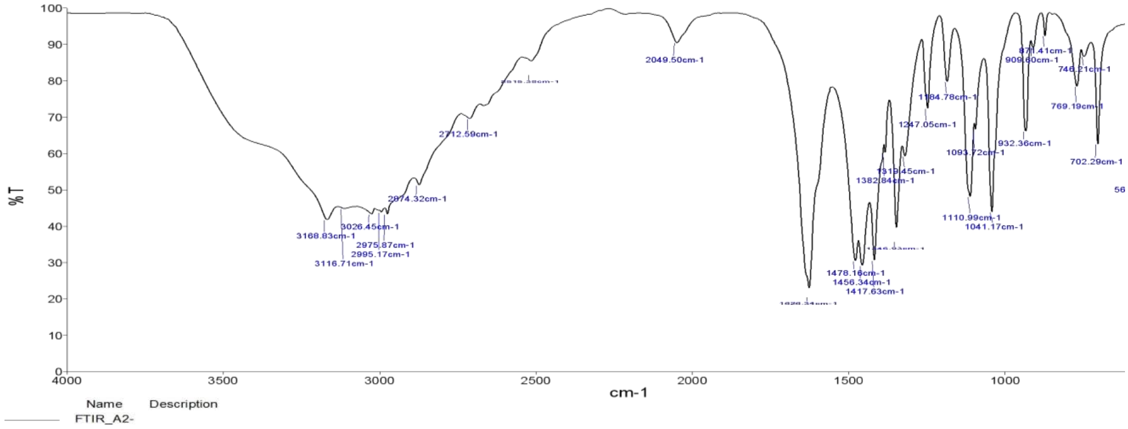

Fig4.FTIR spectrum of 0.002% Methyl Violet doped L Threonine crystal

Table 3. Functional Groups assigned for the peaks.

WAVENUMBER(CM^{-1})	**FUNCTIONALGROUP**
490.12	Stretching vibration of alkylhalides
560.63	C-N Stretching of the amino
702.21	Wagging vibration of CO_2
709.25	C-Cl Stretching
748.43	Bending vibration of CH=CH
908.91and933.36	Stretching vibration of C-O group
1041.20	Stretching vibration of carbon and nitrogen of the amino group
1111.08	Rocking of NH_3
1093.73	C-N Stretching
1184.72	Stretching vibration of C-O
1247.09and1319.48	C-O Stretching
1382.99	CH_2 Vibrations
1417.60	Symmetric structure of CO_2
1456.30	Bending vibration of CH group
2712.60	O-H Stretching

3.ULTRAVIOLET-VISIBLESPECTROSCOPY

In the present work, an attempt was made to analyze optical absorption data obtained on single crystals of pure and Methyl Violet doped L Threonine crystals at room temperature using varian carry 5E, UV -Vis spectrophotometer.

The optical absorption coefficient of the crystals was evaluated using the relation

$\alpha = 2.303 \frac{A}{t}$

where A is absorption, t is the thickness of the crystals.

The optical energy gap (E_g) can be calculated from the well-known quadratic equation which is often called Tauc law.

$\alpha h\nu = A(h\nu - E_g)^n$

where hν= Incident photon energy,

α= Absorption Coefficient,

E_g =Band gap energy of the material,

A= Constant that depends on the electronic transition probability and

n = An exponent that characterize the type of electronic transition responsible [27].

For the optical absorption process can take values 1/2, 3/2, 2, 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. To determine the possible transitions, $(\alpha h\nu)^n$ Versus hν were plotted and corresponding bandgap were obtained from extrapolating the straight portion of the graph on hν axis to zero.

The SHG efficiency of all the grown crystals were determined by Kurtz-Perry powder technique by using Quanta ray model LAB 1710-10 model HG 4 B high efficient. Nd YAG laser was used in the study. The UV absorption spectrum of 1:0.004

dye doped L-Threonine is shown in figure 5 for illustration. The UV–Visible absorption spectrum was recorded in the range 200nm to 800nm. From the spectrum, it is observed that the absorption percentage of L-Threonine crystals increases due to doping and consequently transmittance of doped crystals are less than that of the pure L-Threonine crystals.

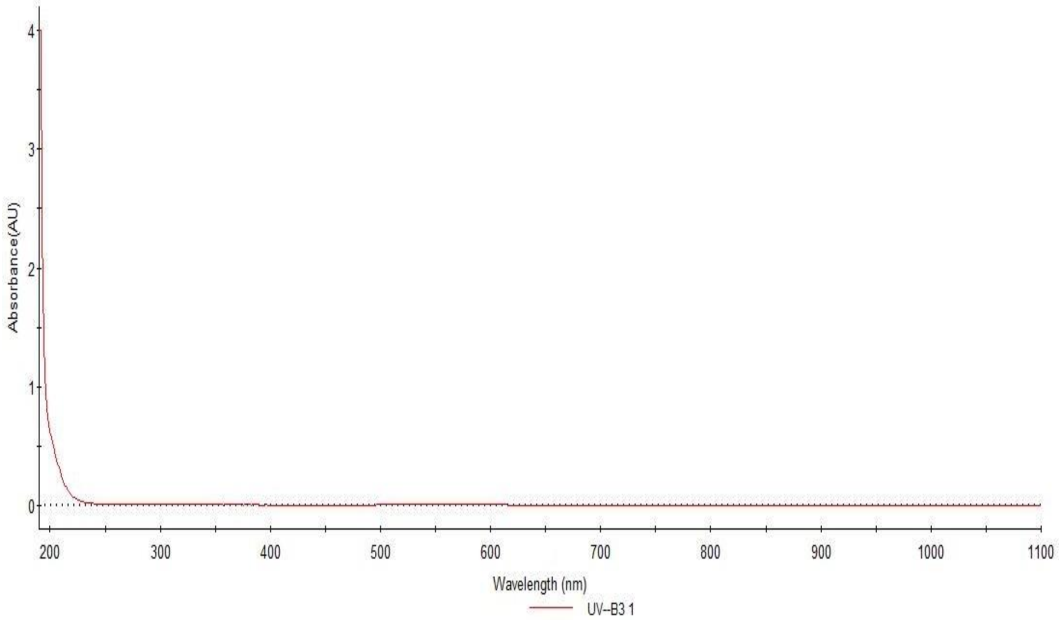

Fig5. UV-Vis spectra of 0.004% Methyl Violet doped L-Threonine crystal

This spectrum shows the full absorption in the entire visible region. So, the pure and Methyl Violet doped L Threonine crystals are very good material for optoelectronic applications. The cut off wavelength were observed from the absorption spectra.

Optical Band Gap:

The optical band gap energy of all the grown crystals were determined from the tauc plot. The tauc plot for the crystal the crystal 1:0.002 Zn doped L-Threonine is shown in figure 6 for illustration.

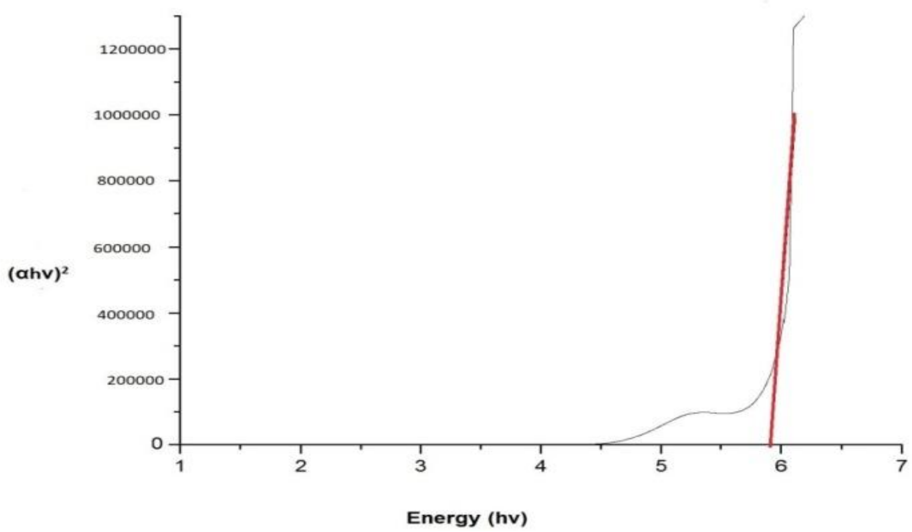

Fig.6.Tauc plot for the crystal 1:0.006 dye doped L-Threonine.

The optical band gap energy for all the grown crystals in the present study are given in table 4.

Table 4: Values of band gap energy

Sl. No.	SYSTEM	λ^{cut} (nm)	E_g(eV)
1	**Pure L-Threonine crystal**	**209**	**5.931**
2	**0.002% Methyl violet doped L-Threonine crystal**	**210**	**5.896**
3	**0.004% Methyl violet doped L-Threonine crystal**	**211**	**5.870**

4	**0.006%Methyl violet doped L-Threonine crystal**	**210**	**5.890**
5	**0.008%Methyl violet doped L-Threonine crystal**	**213**	**5.808**
6	**0.01%Methyl violet doped L-Threonine crystal**	**210**	**5.891**

The band gap energy of pure L Threonine crystal is found to be 5.931 eV. The optical band gap energy of pure L Threonine and Methyl Violet doped L Threonine crystals are almost same. This shows that the doping has no influence on the band gap energies.

Refractive index:
From the UV-Visible spectra, transmittance, reflectance and refractive index are calculated for all the grown crystals.

Transmittance(T) = 10^{-a}
Reflectance(R)=[1-(a+T)]

Refractive index (n)= $\frac{1+\sqrt{R}}{1-\sqrt{R}}$

where a is the absorbance (data).
The variation of refractive index with the incident wavelength of the grown crystals are shown in fig.7.

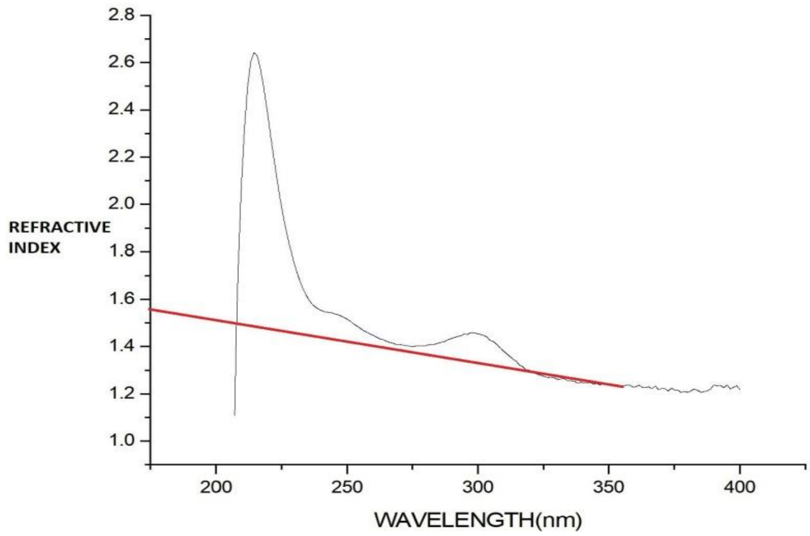

Fig.7.Variation of refractive index with the incident wavelength of the grown crystals are plotted.

The free space dielectric constant [28] can be calculated using the equation,
$\varepsilon_0 = n_o^2$
where ε_0 is the dielectric constant in free space and n_0 is the refractive index which is extrapolated [29]. The n_0 and ε_0 values of all the grown crystals are given in the table 5.

Table 5. n_0 and ε_0 values of all grown crystals.

Sl. No.	**SYSTEM**	**n_0**	**ε_0**
1	**PureL-Threonine crystal**	**1.522 [1.654][18]**	**2.316**
2	**0.002Methyl violet doped L-Threonine crystal**	**1.515**	**2.295**
3	**0.004Methyl violet doped L-Threonine crystal**	**1.441**	**2.076**
4	**0.006Methyl violet doped L-Threonine crystal**	**1.548**	**2.396**
5	**0.008Methyl violet doped L-Threonine crystal**	**1.668**	**2.782**
6	**0.01Methyl violet doped L-Threonine crystal**	**1.557**	**2.424**

The refractive index of grown crystals were almost same with the reference values. The influence of doping concentration has no effect in refractive index.

Table 6. NLO testing report of all the grown crystals.

Sl. No.	**SYSTEM**	**SHGEFFICIENCY (%)**
1	**PureL- Threonine crystal**	**0.372**
2	**0.002%MethylvioletdopedLThreonine crystal**	**NIL**
	0.004%	

3	**0.004% Methyl violet doped L Threonine crystal**	**NIL**
4	**0.006%Methyl violet doped L Threonine crystal**	**NIL**
5	**0.008%Methyl violet doped L Threonine crystal**	**NIL**
6	**0.01%Methyl violet doped L Threonine crystal**	**NIL**

It is found that for pure L Threonine, the SHG efficiency is lower than that of KDP. But the SHG efficiency is absent for the doped crystals. The doped crystals doesn't exhibit NLO property. This is because the organic Methyl Violet is doped with the organic L Threonine. It absorbs all the green colour. Hence the doped crystals doesn't exhibit NLO behaviour. So these doped crystals can be used in the fields of semiconductors, superconductors, photonic crystals, magnetic systems, piezoelectric crystals, ferroelectric crystals etc. [30]

IV.CONCLUSION

All the grown crystals are belongs to orthorhombic system. All the crystals have same band gap energy, refractive index and dielectric constant. The Tauc plot shows the band gap is direct allowed band gap. The SHG efficiency of the doped sample are nil.

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