



A Study Of Growth And Characteristics Of Metal Salt Like Manganese Sulphate [MnSO₄] Doped In L Threonine Amino Acid Single Crystal For NLO Application

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Abstract

L threonine is one of the amino acids exhibiting NLO properties. Study of Manganese sulfate doped in L threonine has been investigated. Pure L threonine and doped with MnSO₄ were grown by slow evaporation method at room temperature. Good quality & transparent crystals were obtained in a month. . The Powder XRD study shows the tetragonal structure with lattice parameter $a = b = 7.506 \text{ \AA}$ and $c = 7.555 \text{ \AA}$. Doping of MnSO₄ in L-threonine crystal was confirmed by FT-IR spectroscopy. NLO properties & hardness testing was executed for grown crystal. Poor SHG efficiency of grown crystal was observed as compared to KDP.

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Keyword: Doping, FT-IR, NLO, Hardness testing, KDP

Introduction

Nonlinear optics play a major role in many of the optical applications such as optical signal processing, optical computers, ultrafast switches, ultra-short pulsed lasers, sensors, laser amplifiers, and many others. In many research work, it was prominently seen that traditional slow evaporation technique at room temperature with water as the solvent was adopted for crystals formation like L Threonine on zinc acetate LTZA [1],[2] bis(L-threonine)zinc(II) (BLTZ) [3], L-threonine phosphate (LTP) [4], L-threonine doped ADP crystals[5], DL-methionine doped ADP crystal[6] L-methionine L-methionine hydrogen maleate (LMMM)[7], dl-methionine hydrochloride[8], L-asparagine monohydrate (LAM) [9],[10], Ammonium Dihydrogen Orthophosphate (ADP) doped with L-Asparagine (LAADP)[11], urea L-asparagine[12] L lysine zinc sulphate [13] were grown successfully. It was also observed in research work that apart from water as solvent, ethyl acetate and hexane also can be used as solvent to grow L-isoleucine with triphosgene [14] Research work done by S. Kalainathan on crystals of L-threonine to determine band gap for all the crystals of L-threonine at different pH 4.40, 5.87 and 6.80. In his experimental work, it was noted that band gap for those crystals were 5.082, 5.247 and 5.193 eV respectively[15]. Similarly, Band gap for Thiourea Ammonium Chloride (TAC) grown crystal by a slow evaporation technique was found 4.327. Both these research paper reveals that wide band gap of the grown crystal do have large transmittance in visible region [16]. Dipak J. Dave found in his research work that doping of amino acids had softened the KDP crystals slightly. He noted that softness of doped KDP crystals is related to load independent micro-hardness. He significantly observed that load independent micro-hardness is maximum to L threonine as compared to other amino acids (L-histidine, L threonine and DL-methionine)[17]. The nonlinear optical properties such as second harmonic generation efficiency and third order susceptibility were studied and were found double on doping the DL-methionine in ADP crystal[6] as compared to pure Potassium dihydrogen phosphate (KDP). In one of study by A. Mostad, DL-methionine

nitrate crystal at higher temperature 121°C shows good NLO properties as its crystal structure shows two centro symmetrically related nitrate groups which were found to be so positioned that one oxygen atom in one group is situated exactly in the direction of the π -orbital of the nitrogen atom in the other group and vice versa [18]. The effect of Fe (III) ion on the stability of the L-asparagine monohydrate (LAM: Fe) crystal in changing temperature through the vibrational spectra was studied and discussed [19]. It was determined that under low temperature conditions the crystal undergoes a conformational transition whereas under high temperatures its structure transforms from the orthorhombic to the monoclinic symmetry and after this process, it goes to an amorphous phase due to the start of the decomposition. Isoleucine malic acid crystals were grown by Elena to note thermal deformations in its crystal structure [20]. It was also revealed that the degree of anisotropy of the crystal structure, thermal expansion of organic compounds was governed by the number and direction of hydrogen bonds. Thus, the value and anisotropy of thermal expansion (or compression) are general characteristics of crystalline materials and can be used to derive correlations of the composition–structure–properties type. It was remarkably pointed that SHG efficiency measurements for L-Isoleucine picrate (LIP) is a highly efficient nonlinear optical (NLO) material having an activity 16 times as that of the reference material potassium dihydrogen phosphate. This LIP crystal is formed by adding L-isoleucine picric acid (1:1) [21]. L-lysine-doped KDP crystals are found to be more beneficial from an application point of view as compared to pure KDP crystals as it was revealed that dielectric constant and the dielectric loss of L-lysine-doped KDP crystals were lower than the pure KDP crystals [22]. Apart from physics point of view, antibacterial studies of L-Lysine single crystals added with potassium bromide were studied out [23]. It was experimental that as compared to L-Lysine, the grown LYPB crystals show a moderate activity against the selected strains of microorganisms in following order as *Staphylococcus aureus* > *Lactobacillus* > *Escherichia coli* > *Salmonella typhi* > *Bacillus subtilis*. Hence the grown LYPB crystals may be considered for pharmacological applications.

NATIONAL STATUS

S. Sahaya Jude Dhas from Kings Engineering College, Chennai, R. Vivekanandhan, K. Raju, V. Chithambaram had grown the organometallic single crystal of LTCC by slow evaporation solution growth technique. Optical studies, DSC studies were carried out on LTCC crystal which confirm its optical window applications in the wavelength region 100 – 1100 nm & can withstand the high temperatures encountered in laser experiments. As noted in same research, LTCC crystal has the efficiency of 1.4 times than that of KDP, which points its applications for optoelectronic devices [24]. G. Ramesh Kumar, Gokul Raj Srinivasan, Rajagopal Mohan, R. Jayavel worked on Growth, structural and spectral analyses of nonlinear optical L-threonine single crystals [25]. It was found that lower UV cutoff wavelength lies at 220 nm in the transmission spectra of l-threonine. Kurtz powder SHG measurements confirm the NLO property of the grown crystal. Microhardness studies have also been carried out on l-threonine crystals. In RMK Engineering College, Sathya Durairaj, V. Sivashankar, P. S. Latha Mageshwari used conventional slow evaporation solution growth technique to synthesize highly transparent solitary nonlinear semi organic optical material Bis(l-threonine) copper (II) monohydrate [BLTCM] single crystals [26]. Thirugnanasambandam Jayanalina from K.S.R. College of Engineering, S. Parthiban, from Annamalai University, S C Mojumdar, Dr G Rajarajan from Vidhya Mandhir Institute of Technology worked on L-Alanine and sodium bromide (LANaBr) crystal which was grown from aqueous solution by a slow evaporation technique. In XRD analysis, the crystalline nature and its various planes of reflections were observed., Vickers microhardness measurement reveals that the crystal is a soft material [27]. M. Suresh, Er. Perumal, Manimekalai College of Engineering, Sultan Asath Bahadur, Kalasalingam University S. Athimoolam Structural, reported and synthesis for first time a new organic second order NLO material: L-isoleucinium p-toluenesulfonate monohydrate (LIPT). The crystal exhibits very good optical properties such as wide optical transparency in the region of 210 nm to 1100 nm and the ultraviolet wavelength emission ($\lambda = 283$ nm). Its second harmonic generation efficiency is found to be 1.7 times the standard KDP. Good thermal, mechanical properties and low dielectric constant at high frequency range show that the grown crystal may be a potential candidate for optoelectronic applications [28]. F. Yogam, Ayya Nadar Janaki Ammal College, I. Vetha Potheher Anna University of Technology, Tiruchirappalli, Jeyasekaran Russalian, Virudhunagar Hindu Nadars' Senthikumara Nadar College, Mark Vimalan, Thirumalai Engineering College, Kilambi, Kanchipuram, India grown single crystal of l-asparagine monohydrate (LAM), organic nonlinear optical material by slow evaporation solution growth technique. The sample was thermally stable up to 125 °C. The photoconductivity study confirms that the LAM crystal has negative photoconducting nature [29]. Mohd. Shkir, King Khalid University, Riscob Bright, Institute for Plasma Research, Kk Maurya, National Physical Laboratory, India had focus on L-asparagine monohydrate (LAM), a new amino acid single crystal grown by slow evaporation solution technique (SEST), The relative second

harmonic generation efficiency was measured and found to be ~ 0.35 times to that of KDP. The laser damage threshold (LDT) was measured and found that the SR crystal has higher LDT value (5.76 GW cm^{-2}) than SEST crystal (4.75 GW cm^{-2}) [30]. S. Natarajan, Madurai Kamaraj University, Neelamagam Rajan Devi, Martin Dhas, Sacred Heart College worked on new organic nonlinear optical (NLO) crystal from the amino acid family, viz., L-methionine L-methioninium hydrogen maleate (LMMM), which was grown by slow evaporation method from aqueous solution. Bulk crystals were grown using a submerged seed solution method. The structure was elucidated using the single crystal x-ray diffraction data. [31]

INTERNATIONAL STATUS

From Brazil, João G. Oliveira Neto, Lincoln A. Cavalcante, Eduardo S. Gomes, Adenilson O. Dos Santos Universidade Federal do Maranhão successfully obtained the crystalline film of LTCu crystal dispersed in Gal solution by the technique of solvent slow evaporation at low temperature. By means of XRD, it was observed that the crystallinity was proportional to the addition of LTCu crystals. The TG-DTA revealed low thermal stability of the crystal due to the exit of water molecules with the increase of temperature [32]. From Pakistan, Ferdousi Akhtar and Jiban Podder harvested optically transparent, large size and electrically conducting LA crystal in a laboratory for useful application in optoelectronic devices. The chemical composition of the grown optically transparent LA crystals was determined by Energy Dispersive X-ray (EDX) and Fourier Transform Infrared (FTIR) Spectroscopy. [33]. From Shanghai Ocean University Jianan Chen, Xiaoqin Li, Dianyu Huan, Wenxiang Yao studied comparison of the supplemental effects of crystalline DL methionine (DLMet) and methionine hydroxy analogue calcium (MHACa) on growth performance of Pacific white shrimp. [34]. From China, Yujing Bian, Xun Zhang, Zhenqi Zhu, Bin Yang, the terahertz absorption spectra of L-Lysine (Lys) and L-Lysine hydrate (Lys•H₂O) crystals have been measured by terahertz time-domain spectroscopy (THz-TDS) at the range of 0.3-2.5 THz under room temperature. Therefore, the combination of THz-TDS technology and PED analysis opens up an opportunity for identifying Lys and its hydrate, which provides a theoretical reference for studying vibrational modes of biomolecules [35]. From University Federal do Maranhão, Brazil, R. J. C. Lima, E. C. Santos-Junior, A. J. D. Moreno, P. F. Façanha-Filho, P. T. C. Freire & M. I. Yoshida performed thermogravimetric analysis and differential thermal analysis of the L-alanine, taurine, and L-threonine crystals at high temperatures. No clear correlation between the hydrogen bonding strengths and endothermic peak positions was observed. [36].

STUDY HYPOTHESIS

Nonlinear optical (NLO) crystals play an important role in area of material fabrication, contemporary devices and laser technology. It is noted from previous research work that the presence of the amino acids stabilizes crystal polymorph [37] as well as were found more effective in inhibiting crystal growth [38]. Amino acid crystals are generally known for its NLO property too. With the hypothesis that metal salts mixed with Amino acid from the aspartate family may show better NLO properties, so its crystals grow, its characteristics are emphasized in this present research work.

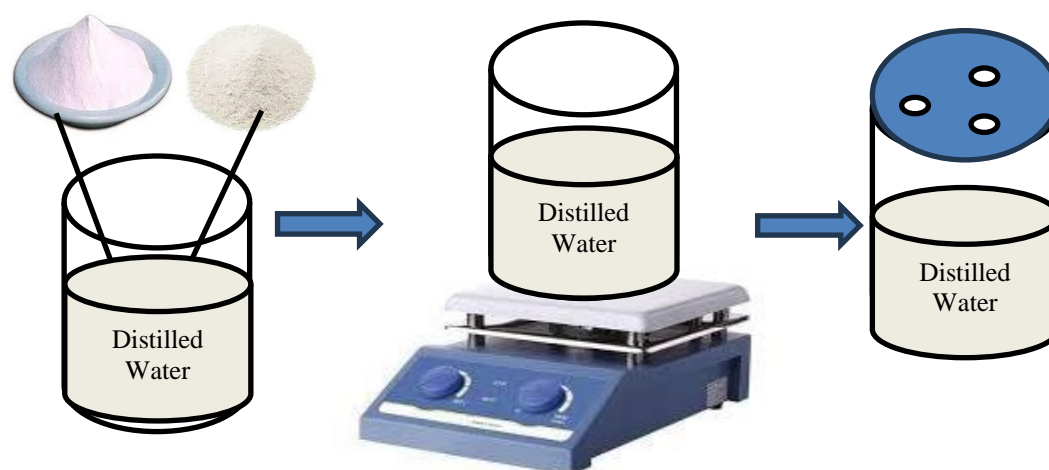
STUDY RATIONALE

Nonlinear optics (NLO) is the branch of optics which explains nonlinear response of incident light properties like frequency, polarization, phase or path. These nonlinear responses give rise to a host of optical phenomena such as Second Harmonic Generation, Third Harmonic generation, High Harmonic Generation, optical parametric amplification, Self-phase modulation, self-diffraction, cross phase modulation etc. These nonlinear optical phenomena are base of many components of optical communication systems, optical sensing and material research. Materials used for Nonlinear optics highly transmits at the fundamental and harmonic wavelengths having a high laser induced damage threshold to allowing optical intensities to provide adequate conversion efficiency. Such materials are referred as NLO materials. Examples of NLO materials are Barium borate, cadmium lithium borate, lithium iodate, Monopotassium phosphate, zinc oxide, Tellurium dioxide [39]. These NLO Crystals are further categories to Inorganic NLO - eg KCL, lithium niobate (LiNbO₃) or potassium dihydrogen phosphate (KH₂PO₄), KDP, (KTiOPO₄), Barium metaborate, Methyl parahydroxyl benzoate e.t.c [40],[41]. Organic NLO crystal - 4-dimethylamino-N-methyl-4-stilbazolium-tosylate (DAST), 2-(3-(4-hydroxystyryl)-5,5-dimethylcyclohex-2-enylidene)malononitrile OH₁ [42]. Semi organic NLO crystal - BTCC: Bis(thiourea) cadmium chloride, Bis-thiourea cobalt chloride (BTCOC), ATCC triallyl thiourea cadmium chloride, ATMB Triallyl thiourea mercury bromide, TSCCB thiosemicarbazide cadmium bromide, zinc

thiourea chloride (ZTC) , 4-aminophenyl)sulphonyloxy)zinc(II)chloride Crystal [43],[44],[45],[46],[47] [48], Various techniques like solvent evaporation, slow cooling of the solution, solvent/ non-solvent diffusion, vapor diffusion and sublimation for crystals formation of NLO materials [1],[2],[3],[4],[5],[6],[7],[8],[9],[10],[11],[12],[13],[25],[26],[27],[30],[31],[32],[33]. Due to chiral carbon atom and no centrosymmetric space group, an Amino acid crystal has excellent NLO and electro optical properties. Biosynthesis pathway in bacteria & plants categorizes Amino Acid to six families as Histidine, Aromatic, pyruvate, serine, aspartate, glutamate family respectively [49]. The Aspartate family has 5 essential amino acids like lysine, asparagine, methionine, threonine and isoleucine. Research work was carried on mixing amino acid with heavy metal like L threonine with cadmium chloride[50], cadmium acetate [51], leucine mixed with copper[52] where it was reveal those grown crystal showed good transparency, low cutoff wavelength from UV studies. This gives appeal to use for optoelectronics devices. These observations provoke the growth of crystals of the amino acid with metal salt to check enhancement of NLO properties for its applications in optoelectronics devices.

RESEARCH METHODOLOGY

Slow evaporation method was adopted to prepare crystals of L threonine Manganese sulphate from aqueous solution. Equimolar ratio of supersaturated solution of L threonine and Manganese sulphate were mixed for 30 minutes in distilled water at room temperature. Solution was further filtered using whatman filter paper which was further kept in a beaker covered with aluminum paper with few holes pierced in it for slow evaporation. The Crystals were grown in 45 days by slow evaporation.



Magnetic stirring for 30 minutes at room temperature

CHARACTERIZATION TECHNIQUES

The qualitative analysis of the grown crystal was carried out by characterization studies to assess the physical and chemical properties of the material for improving the quality of the crystal. In the present work, the grown crystal was subjected to the following characterization studies:

- 1) Crystal structure analysis by powder and single crystal XRD techniques using PerkinElmer Spectrum IR Version 10.7.2
- 2) PL analysis was studied using JASCO Spectrofluorometer Model - FP-8300 WRE to investigate the quality of grown crystals.
- 3) NLO test to confirm the nonlinear behavior of the material and to estimate the SHG efficiency using Q switched High Energy Nd:YAG Laser (QUANTA RAY Model LAB – 170 - 10) Model HG-4B
- 4) Laser Threshold Damage The laser threshold damage (LDT) of NLO crystal is defined as a measure of crystal surface damage under the influence of high-power laser beam using Q - switched High Energy Nd:YAG Laser (QUANTA RAY Model: LAB – 170 - 10)
- 5) FTIR was studied using PerkinElmer Spectrum IR Version 10.7.2

RESULTS AND DISCUSSION

XRD

X-ray powder diffraction (XRD) technique was used to ascertain the purity of the grown crystal. The positions of the peaks were found to be in good agreement with the standard data. Experimental and standard d values, intensity ratio and hkl values of L-threonine crystals analyzed from powder XRD pattern are presented in Table 1. The change in diffraction peaks intensity indicating the presence of dopant in L threonine. All the crystals are belonged to body centered tetragonal structure symmetry

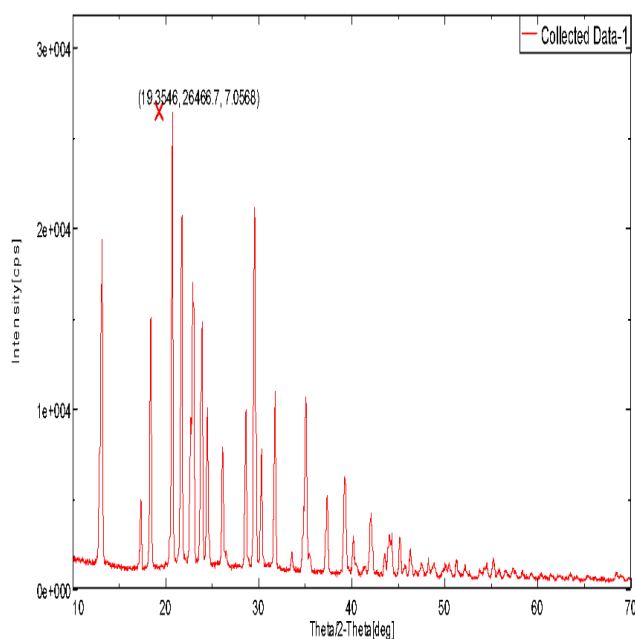


Fig 1 : XRD of L threonine

h	k	l	2-theta (deg)	d(ang.)	Int. I (counts deg)
1	1	0	13.1583	6.72305	666.12
2	1	0	17.3338	5.1118	130.24
1	0	1	18.4074	4.81602	526.92
0	1	1	20.5905	4.31006	111.65
1	1	1	21.5967	4.11148	493.79
0	2	0	22.7346	3.9082	276.95
1	2	0	23.8717	3.72454	495.71
4	1	0	28.6433	3.11401	319.85
1	2	1	29.5281	3.02268	613.23
3	2	0	30.3427	2.94336	235.54
2	2	1	31.7507	2.81597	351.81
4	1	1	33.5833	2.66638	32.1
1	1	2	37.3333	2.40672	185.47
4	2	1	39.185	2.29714	192.61

Table 1: Miller Indices of L threonine

The appearance of sharp and strong peaks confirms the good quality of the grown crystal

Photoluminescence study PL

To investigate the quality of grown crystals, the qualitative measurement of impurity incorporation and the optical phenomena like recombination of the electron transitions, the photoluminescence emission study at

particular wavelength becomes a pioneer technique. The PL excitation wavelength is 254 nm and emission wavelength is 280 nm. The spectra exhibit two emission peaks at different wavelengths, as listed in Table 5.

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sample	Emission wavelength	
Pure ADP	367.92 nm	469.94 nm[53]
ADP + 0.4 wt threonine	365.90 nm	468.93 nm
This work	300 nm	

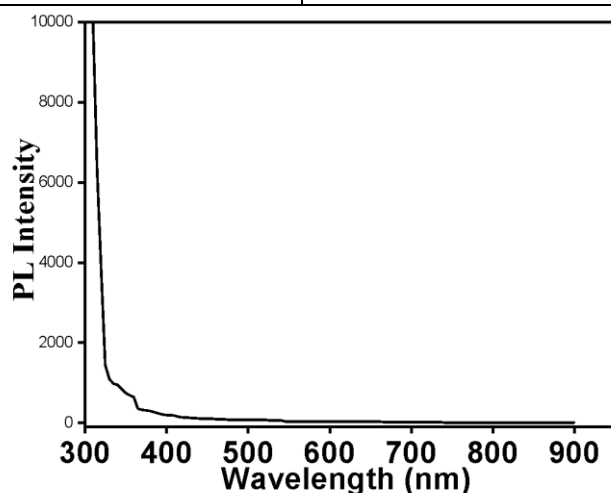


Fig 2: PL

Table 2:FTIR

Wavenumber cm^{-1}	Vibrational assignments
3157	NH ₃ ⁺ asymmetric stretching
2978	NH ₃ ⁺ symmetric stretching
2866	C-H symmetric stretching
1628	NH ₃ ⁺ asymmetric deformation
1483	NH ₃ ⁺ symmetric deformation
1417	COO ⁻ asymmetric stretching
1110	NH ₃ ⁺ rocking
561	C-C-N deformation

[54],[55] The Fig. 4 shows the FTIR Spectrum of L Threonine manganese sulfate. Fourier transform infrared studies (FTIR) were used to confirm the presence of various functional groups in the crystals

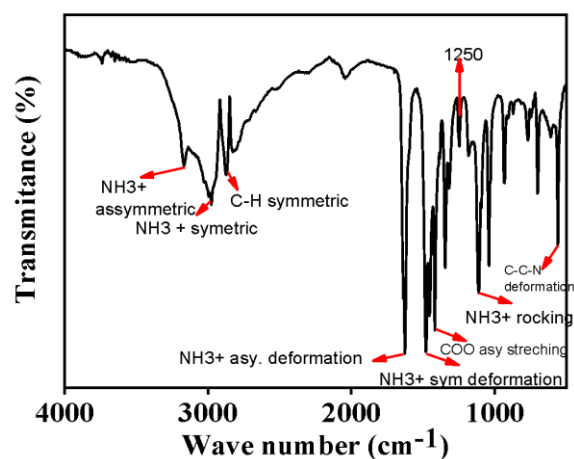


Table : Vibrational assignments of L Threonine Manganese Sulfate crystal

The force constant was calculated for OAH vibration, presently. The relation between the absorption frequency and the force constant can be written as,

$$\nu = 1330 \sqrt{F \left(\frac{1}{M_1} + \frac{1}{M_2} \right)}$$

where ν = Absorption frequency (cm⁻¹), 1330 = (NA X 10)^{1/2} / 2 π C, NA = Avogadro's number, F = Force constant (N m⁻¹), M₁ and M₂ = Molecular masses of atoms (u). From Table 3 it can be seen that the force constant gets altered as the amino acids interact with the hydrogen bond of ADP.

Sample	Force constant	absorption
Pure ADP	526	3135
ADP + 0.4 % wt L threonine	534	3156
This work		

Table 3 Force constant of O-H vibration for pure and L-threonine doped ADP crystal.

Laser threshold damage (LDT) study

The laser threshold damage (LDT) of an NLO crystal is defined as a measure of crystal surface damage under the influence of a high-power laser beam. This study involves optical processes like electron avalanche, multi photon absorption and photo ionization for NLO crystals.

Damage of calculated values for Laser Threshold damage for pure L threonine is tabulated in table. It is observed that thickness 0.5 mm was damaged at 82.3 mJ.

Laser Damage Threshold Values

Sl. No.	Thickness Mm	Energy (E)milli joule	Observation
1	0.5	82.3	Damaged

Nd:YAG Laser used for LDT studies having Wavelength (λ) = 1064 nm, Focal Length of the Biconvex Lens (f) = 10 cm, Pulse width (τ) = 6 , Repetition rate: 10 Hz. **Energy was measured by** EPM 2000.Model: J-50-MB-YAG having energy range from 1.5 mJ to 3 J

	NLO material	LDT value (GW/cm ²)
1	KDP	0.2[2][56]
2	BLTCM	0.6[3] [57]
4	Ltheorinine manganese sulfate	This work

NLO testing reports

Second harmonic studies of Grown crystal were studied using Kurtz powder techniques. Fine powder of crystal was tightly packed in a microcapillary tube. Further it was exposed to Incident wavelength of the light: 1064 nm, Wavelength of the light emitted from the sample: 532 nm , Repetition rate: 10 Hz ,Pulse width: 6 ns, with input energy of 0.7 joule. Energy of 4.5 mJ for output light was detected.. SHG conversion efficiency was calculated by taking the ratio of output energy of the sample with respect to that of KDP having the same input energy.SHG efficiency of sample was half. As compared to KDP. The decreased SHG efficiency is due to lower polarizability of the material than that of KDP.

Sl. No	Sample Code	Output Energy(milli joule)	Input Energy (joule)	SHG
1	KDP (Reference)	8.94	0.70	12.77
2	L threonine	5.24	0.70	7.24
3	L threonine MnSO ₄ (1:1)	4.50	0.70	6.42

Conclusions:

Single crystals of L-Threonine manganese sulfate were grown by slow evaporation technique. Crystal structure, functional groups of crystal are confirmed by XRD, FTIR.Crystal was observed to be damaged by 8.23 mJ by Laser Damage testing. SHG efficiency of studied crystals showed poor efficiency than KDP.

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