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Research Article

Enhancement of SHG, Spectral, Optical, Thermal, Dielectric and Mechanical Properties of Methylene Blue Admixtured L-Alanine Thiourea Single Crystal

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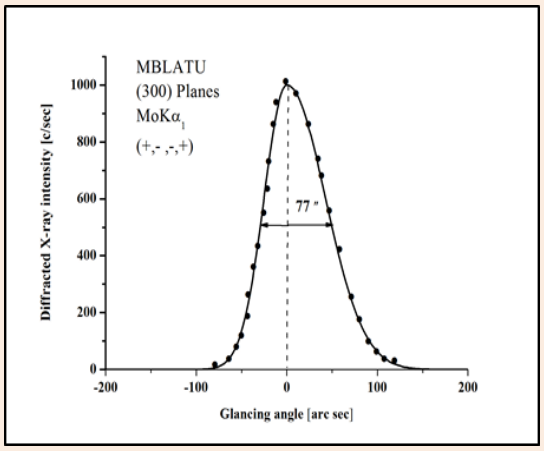
Abstract

L-Alanine Thiourea (LATU) and methylene blue dye admixtured LATU(MBLATU) single crystals were grown by slow evaporation method under isothermal condition. The grown crystals were subjected to single crystal X-ray diffraction and powder X-Ray diffraction analyses to determine the crystallographic parameters. HRXRD analysis reveals the presence of methylene blue dye in interstitial site of LATU crystal lattice and it confirms the crystalline perfection of grown crystals. The functional groups present in the crystals were confirmed by FTIR analysis. The UV-vis-NIR transmission studies show the optical transparency in the entire visible region of methylene blue dye admixtured LATU crystal. The crystals were further subjected to other important characterizations such as dielectric measurement, micro hardness, thermal and NLO studies.



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Keywords: LATU, MBLATU, FTIR, slow evaporation, methylene blue dye, X-ray diffraction, UV-vis-NIR spectrum, NLO study

Introduction

In the recent years, nonlinear optical(NLO) crystals have attracted the researchers due to their potential applications in the fields of high-energy lasers for inertial confinement fusion research [1], electro-optic switches, frequency conversion [2], colour display and photonics including optical information processing [3-6]. Organic materials have been known for their potential applications in semiconductors, superconductors and nonlinear optical devices [7]. Thiourea is a centro symmetric molecule and has the ability to form an extensive network of hydrogen bonds [8]. The Centro symmetric Thiourea molecule when combined with amino acids yields non-centrosymmetric complexes, which possess in general good nonlinear optical properties. Some of the nonlinear crystals of the amino acid complexes of Thiourea reported are glycine Thiourea [9] and L-HistidineThiourea [10]. Among these the second harmonic generation efficiency (SHG) of glycine Thiourea crystal was 0.5 times that of KDP and the SHG efficiency of L-Histidine Thiourea crystal 4.1 times that of KDP. Many researchers have worked on dye admixtured potassium dihydrogen phosphate and potassium acid phthalate nonlinear optical crystals in order to improve their nonlinear response [11, 12]. Among all the organic dyes, methylene blue is of particular interest due to its susceptible behaviour to the surface enhancement of the second order nonlinearity as it is near centrosymmetric, with centrosymmetry broken in the direction orthogonal to π conjugation. The measured hyperpolarizability of methylene blue molecules in aqueous solution is 198 x 10^{-30} esu [13]. Methylene blue, belonging to a thiazene class of dyes, is also known as methylthionine chloride. It has the molecular formula $C_{16}H_{18}ClN_3S$. It is stable under ordinary conditions. Hence the admixture of methylene blue in LATU crystals is expected to have high second order

nonlinearity. In the present investigation, a comparative study on the growth, structural, UV-vis-NIR transmission, thermal, dielectric, mechanical and non-linear optical studies of pure and methylene blue dye admixtured LATU crystals have been reported.

Experimental Procedure

Synthesis and Crystal Growth

L-Alanine Thiourea(LATU) was synthesized by dissolving high purity Thiourea and L-Alanine in the equimolar ratio in aqueous medium. Thiourea was first dissolved in millipore water and then L-Alanine was added with continuous stirring for about 2 hours using a magnetic stirrer at 50 ˚C . The product was obtained as per the following reaction.

$$H_2N\text{-}CS\text{-}NH_2 + CH_3CHNH_2COOH \rightarrow H_2N\text{-}CS\text{-}NH_3^- CH_3CHNH_2COO^+$$

(Thiourea + L-Alanine → L-Alanine Thiourea)

The impurity content of L-Alanine Thiourea(LATU) was minimized by the process of recrystallization. The pH value of the solution was about 7.24. The pH value was adjusted to 3.5 by adding few drops concentrated hydrochloric acid [14]. Then it was filtered using Whatmann filter paper and the filtered solution was kept in a borosil beaker covered with an aluminium foil and the solvent was allowed to evaporate at room temperature. As a result of slow evaporation, after 30 days, colourless and transparent LATU crystal with dimensions of 12×3×3 mm^3 was obtained. The same experimental procedure was adopted for the synthesis of methylene blue dye (5 mol %) admixtured LATU salt and the seed crystal with perfect shape and free from macro defects was used for the growth of dye admixtured LATU crystal by slow evaporation method. The photographs of pure LATU and methylene blue dye admixtured LATU(MBLATU) crystals are shown in **figure 1** and **figure 2**.

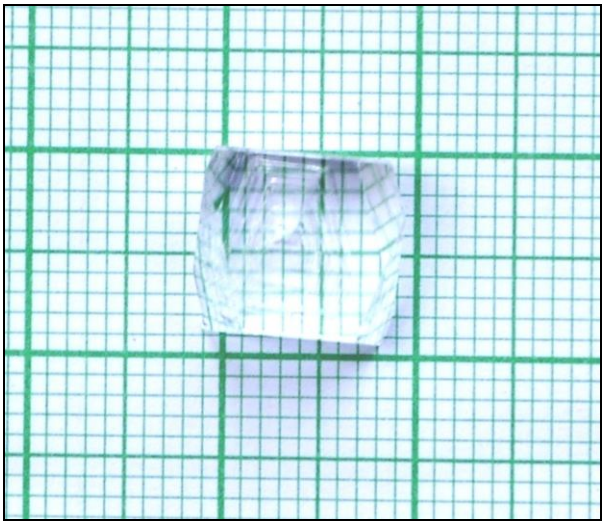

Figure 1 Grown LATU crystal

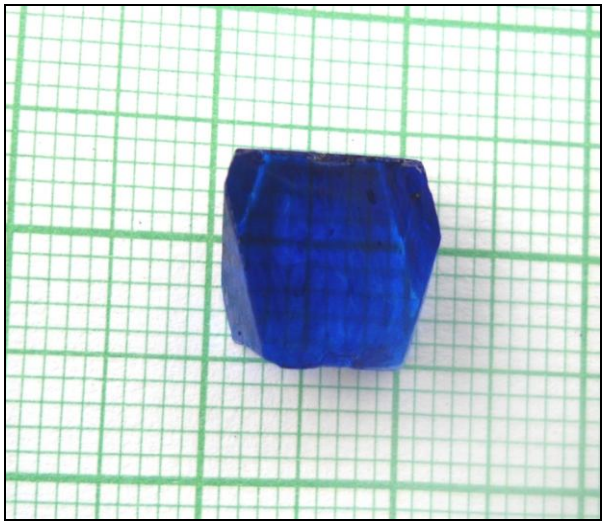

Figure 2 Grown MBLATU crystal

Results and Discussion

Single crystal XRD analysis

The single crystal XRD analysis of LATU and methylene blue dye admixtured LATU(MBLATU) crystals were carried out using MESSRS ENRAF NONIUS CAD4-F, single X-ray diffractometer with MoKα (λ=0.71073 Å)

radiation. The lattice parameters of LATU and MBLATU crystals obtained from single crystal XRD analysis are presented in **table 1**.

Table 1 Comparison of lattice parameters of LATU and MBLATU

S. No.	Crystal name	Axial lengths of unit cell (a, b and c)	Inter axial angles (α, β and γ)	Volume	Crystal system	Space group
01.	LATU	a = 9.6312 Å b = 5.6136 Å c = 9.4142 Å	α= γ =90° β =109.48°	508.98 $Å^3$	Monoclinic	$P2_1$
02.	MBLATU	a = 9.6401 Å b = 5.6150 Å c = 9.4202 Å	α= γ =90° β =109.48°	509.90 $Å^3$	Monoclinic	$P2_1$

The single crystal XRD study reveals that the presence of dopant has not altered the basic structure of the LATU crystal. The lattice parameter values of methylene blue admixtured crystal may be attributed to the lattice strain in the grown crystals due to the incorporation of the dye dopant.

Powder XRD Analysis

The grown crystals of LATU and MBLATU were crushed into fine powder and powder X-ray diffraction analysis has been carried out using Rich Seifert X-ray diffractometer. The X-axis of graph is 2θ. The Y-axis gives the intensity in arbitrary units. The samples were subjected to intense X-ray of wavelength 1.5406 Å (CuKα) at a scan speed of 1°/minute to obtain lattice parameters. The Miller indices (hkl), d-spacing and diffraction angle (2θ) are summarized for LATU and MBLATU are shown in **table 2** and **table 3** with the help of RexCell software program and their powder diffractograms are shown in **figure 3** and **figure 4**.

Table 2 Miller indices, d-spacing and 2θ-values of L-Alanine Thiourea(LATU) single crystal determined from powder XRD analysis using RexCell software

S. No.	h	k	l	d (obs) (A°)	d (cal) (A°)	2θ (obs) (deg)	2θ (cal) (deg)
1	2	0	-1	4.59282	4.59479	19.303	19.294
2	1	0	-2	4.28883	4.28477	20.685	20.705
3	1	1	1	3.81913	3.81395	23.263	23.295
4	2	1	0	3.48218	3.48090	25.550	25.560
5	3	0	-1	3.13881	3.13725	28.401	28.415
6	2	1	-2	3.07372	3.07392	29.015	29.014
7	2	1	1	2.93698	2.93525	30.398	30.417
8	1	1	2	2.84657	2.84937	31.388	31.357
9	3	1	-1	2.73649	2.73839	32.685	32.662
10	3	0	1	2.52323	2.52358	35.536	35.531
11	1	2	1	2.46934	2.46928	36.338	36.339
12	0	2	2	2.31055	2.31088	38.933	38.927

Table 3 Miller indices, d-spacing and 2θ-values of methylene blue dye admixtured LATU(MALATU) single crystal determined from powder XRD analysis using RexCell software

S. No.	h	k	l	d (obs) (A°)	d (cal) (A°)	2θ (obs) (deg)	2θ (cal) (deg)
1	0	1	1	4.60490	4.60990	19.252	19.231
2	1	0	1	4.44116	4.44892	19.969	19.933
3	2	0	0	3.82467	3.83088	23.229	23.191
4	2	1	0	3.49136	3.49537	25.482	25.452
5	2	0	-1	3.14808	3.14339	28.316	28.359
6	1	2	-1	3.08080	3.08494	28.947	28.908
7	2	1	1	2.94344	2.94273	30.330	30.337
8	0	3	0	2.84808	2.84694	31.371	31.384
9	0	0	2	2.73927	2.73804	32.651	32.666
10	0	3	1	2.52441	2.52597	35.519	35.496
11	1	1	-2	2.47159	2.47045	36.304	36.322
12	3	0	1	2.31347	2.31196	38.882	38.908
13	2	1	-2	2.15674	2.15829	41.835	41.803
14	3	2	1	2.03440	2.03312	44.480	44.510
15	1	4	-1	1.92617	1.92599	47.126	47.131

From the X-ray powder diffraction data, the lattice parameters for MBLATU were found to be a = 9.610 Å, b = 5.5871 Å and c = 9.4249 Å. This is in close agreement with the values obtained from single crystal X-ray diffraction analysis for MBLATU. The change in intensity of peaks as well as addition in number of peaks for MBLATU crystal in the powder X-ray diffraction pattern reveal that the dye doped crystal is slightly distorted compared to the pure LATU crystal. This may be attributed to strains on the lattice by the absorption or substitution of methylene blue dye in LATU crystal.

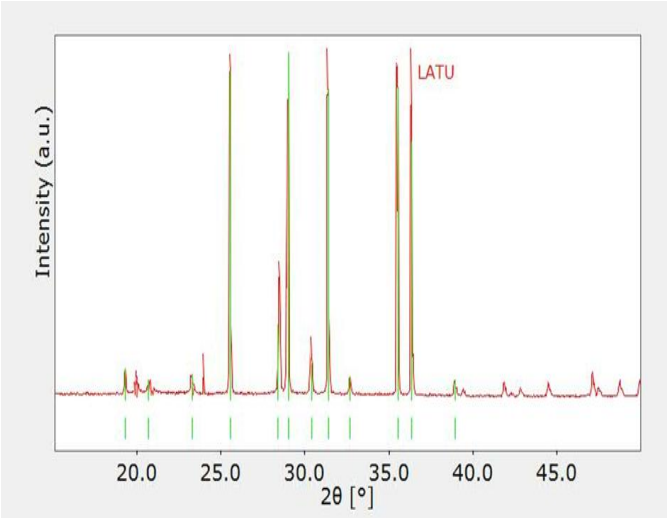

Figure 3 PWXRD spectrum of LATU crystal

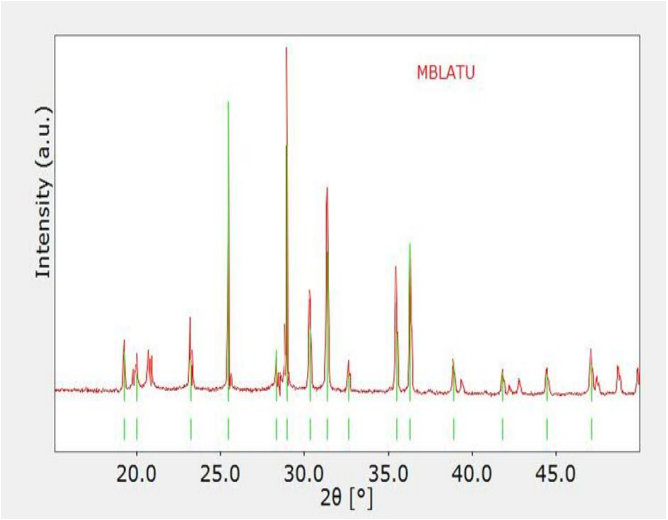

Figure 4 PWXRD spectrum of MALATU crystal

High resolution X-ray diffraction studies

The crystalline perfection of the grown crystals were characterized by HRXRD analysis by employing a multicrystal X - ray diffractometer with MoKα_1 radiation designed and developed at National Physical Laboratory (NPL) New Delhi [15] has been used to record high-resolution diffraction curves (DCs). The well-collimated and monochromated MoKα_1 beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,- ,-,+) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. Before recording the diffraction curve, to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity, the pure LATU and methylene blue dye admixtured LATU crystals were first lapped and chemically etched in a non-referential etchant of water and acetone mixture in 1:2 ratios. **Figure 5** and **Figure 6** show the high-resolution diffraction curves (DCs) recorded for pure LATU and methylene blue dye admixtured LATU crystals using (3 0 0) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with MoKα_1 radiation.

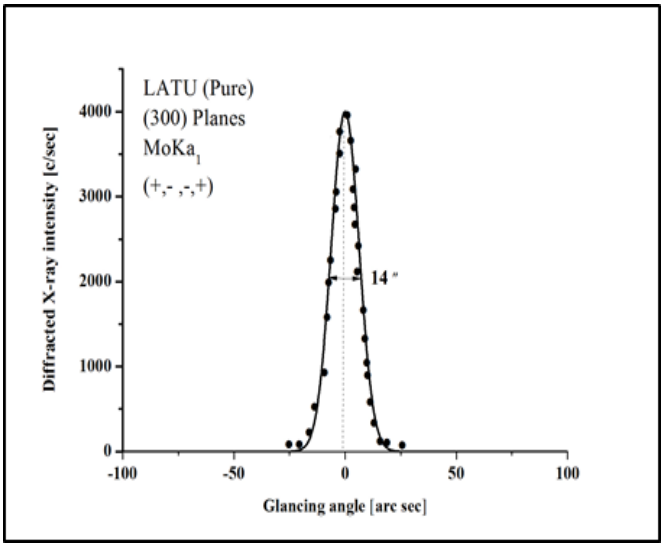

Figure 5 HRXRD curve of pure LATU crystal

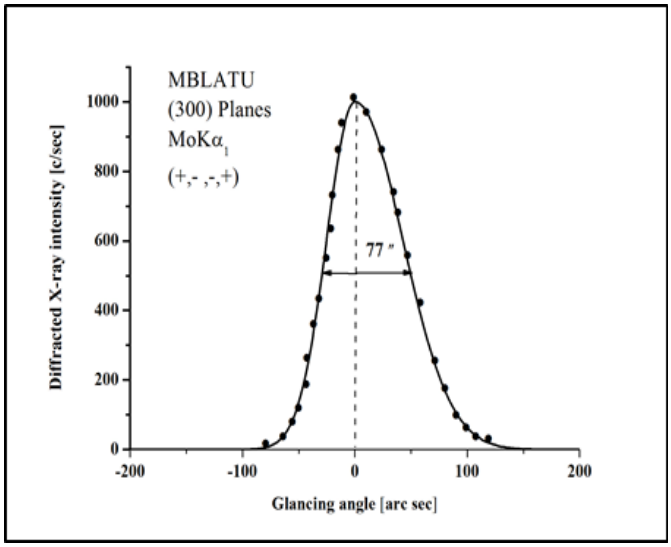

Figure 6 HRXRD curve of MBLATU crystal

The curves are very sharp having full width at half maximum (FWHM) of 14 arc sec for pure LATU and 77 arc sec for methylene blue dye admixtured LATU crystals as expected for nearly perfect crystals from the plane wave dynamical theory of X-ray diffraction [16]. The absence of additional peaks and the very sharp DC shows that the crystalline perfection of the specimen crystals is extremely good without having any internal structural grain boundaries and mosaic nature. The increase in FWHM without having any additional peaks in DC of methylene blue dye doped LATU crystal indicates the incorporation of methylene blue dye in the crystalline matrix of LATU crystal. In DC of methylene blue dye doped LATU crystal, for a particular angular deviation($\Delta\theta$) of glancing angle(θ) with respect to the Bragg peak position (taken as zero for the sake of convenience), the scattered intensity is much more in the positive direction in comparison to that of the negative direction. This feature or asymmetry in the scattered intensity clearly indicates that the methylene blue dopants predominantly occupy the interstitial positions in the lattice and elucidates the ability of accommodation of dopants in the crystalline matrix of the LATU crystal. This can be well understood by the fact that due to incorporation of dopants in the interstitial positions, the lattice around the dopants compresses and the lattice parameter d (interplanar spacing) decreases and leads to give more scattered (also known as diffuse X-ray scattering) intensity at slightly higher Bragg angles(θ_B) as d and sin θ_B are inversely proportional to each other in the Bragg equation ($2d \sin\theta_B = n\lambda$; n and λ being the order of reflection and wavelength respectively which are fixed). It may be mentioned here that the variation in lattice parameter is only confined very close to the

defect core which gives only the scattered intensity close to the Bragg peak. Long range order could not be expected and hence change in the lattice parameter is also not expected [17]. The HRXRD results confirm an important finding that methylene blue dye entrapped in the LATU crystals, but the amount is limited to a critical value and above which the crystals have a tendency to develop structural grain boundaries [18].

Fourier Transform Infrared Spectroscopy

The FTIR spectra of pure and dye admixtured LATU crystals are shown in **figure 7** and **figure 8**.

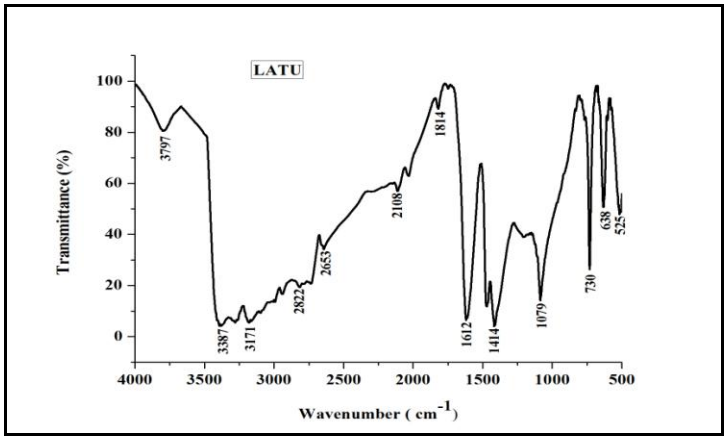

Figure 7 FTIR spectrum of grown L-Alanine Thiourea (LATU) single crystal

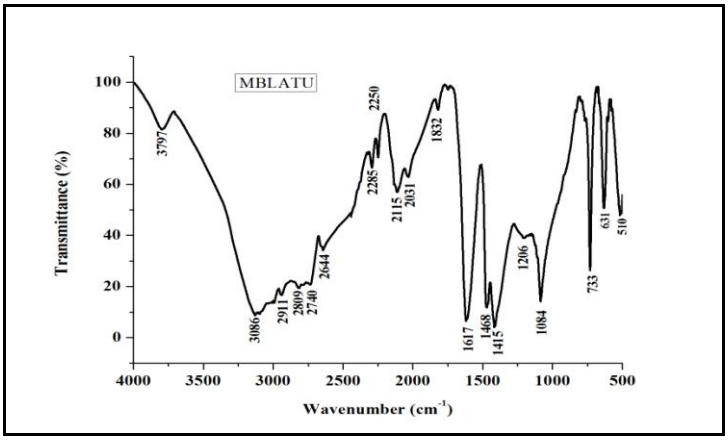

Figure 8 FTIR spectrum of grown methylene blue dye admixtured LATU (MALATU) single crystal

The incorporation of methylene blue dye in LATU crystal has been strongly verified by spectral analysis. The O-H stretching due to water of crystallization arises at frequencies of 3797 cm^{-1}, 2911 cm^{-1}, 2740 cm^{-1}, 2285 cm^{-1} and at 2250 cm^{-1} in LATU and methylene blue dye doped LATU crystals spectra respectively. In the methylene blue admixtured LATU spectrum, the OH stretching in the high energy region is very much broadened due to hydrogen bonding. The broad band confirms the presence of methylene blue in LATU. Very strong band occurring at 510 cm^{-1} is contributed by S-C-N symmetric bending vibration. The vibration frequencies of L-Alanine Thiourea are compared with methylene blue dye admixtured L-Alanine Thiourea in **table 4** to confirm the incorporation of methylene blue dye in LATU crystal.

Table 4 Functional group assignments of L-Alanine Thiourea (LATU) and methylene blue dye admixtured LATU (MBLATU) crystals

S. No.	L-Alanine Thiourea (LATU)	Methylene blue dye admixtured LATU (MBLATU)	Assignments
	Wavenumber (cm^{-1})		
1	3797	3797	OH - stretching
2	3387	-	N-H stretching
3	3171	3086	=CH stretching
4	2822	2809	Aliphatic (C-H) stretching
5	2653	2644	C-H symmetric stretching
6	2108	2115	Over tone region with a combination of symmetric NH_3^+ bending and torsional vibrations.
7	1814	1832	C=O absorption
8	1612	1617	NH_3^+ bending vibrations
9	1414	1415	N-C-N stretching
10	1079	1084	CH_3 rocking
11	730	733	C=S stretching
12	638	631	(C-H) bending
13	525	510	S-C-N symmetric bending

UV-visible spectral study

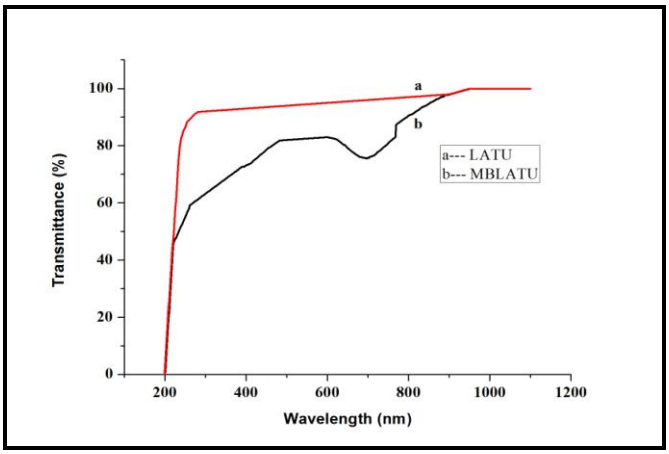

Figure 9 UV-vis-NIR absorption spectra of LATU and MBLATU crystals

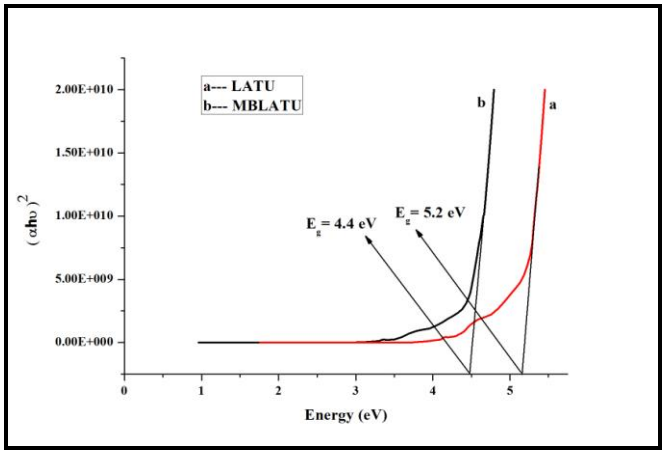

Figure 10 Photon energy vs $(\alpha h\upsilon)^2$ for LATU and MBLATU crystals

The UV-visible spectra of pure and methylene blue dye admixtured analyses have been carried out using Shimadzu UV-visible spectrophotometer in the wavelength range of 100-1100 nm. Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window [19]. The optical transmission spectra recorded for LATU and MBLATU are shown in **figure 9** and **figure10**.

The cut-off wavelengths of pure and admixtured LATU crystals are found to be 209 nm and 691 nm. It is observed that the transparency of dye admixtured LATU crystal decreases in comparison with that of pure LATU and the shift of lower cut off wavelength in UV region is due to addition of methylene blue dye in the LATU crystal. This is very important for materials possessing nonlinear optical properties.

Optical band gap energy (E_g) calculation

The band gap energy of the pure and methylene blue dye admixtured LATU crystals were calculated from the **figure 10** by taking Photon energy (hν) values along X-axis and $(\alpha h\nu)^2$ values along Y-axis for LATU and MBLATU crystals. The optical absorption coefficient (α) was calculated using the relation

$$\alpha = (2.3026 * \log (1/T)) / t \quad (1)$$

Where, T is the transmittance and t is the thickness of the crystal. The band gap energy values were calculated by extrapolation of the linear part of the curve for LATU and MBLATU and found to be 5.2 eV and 4.4 eV respectively. The decrease in band gap energy value of dye admixtured LATU may be due to incorporation of dye in the LATU crystal lattices. The value of band gap energy for MBLATU crystal suggests that the material is dielectric in nature to possess wide transmission range. The large transmission in the entire visible region and lower cut off wavelength enable it to be a potential material for second and third harmonic generation [20].

Thermo gravimetric analysis (TGA)

Thermo Gravimetric Analysis(TGA) and Differential Thermal Analysis(DTA) were carried out for LATU and MBLATU crystals using TA Q-500 analyzer. TGA and DTA curves for pure and methylene blue dye admixtured LATU are shown in **figure 11** and **figure 12**.

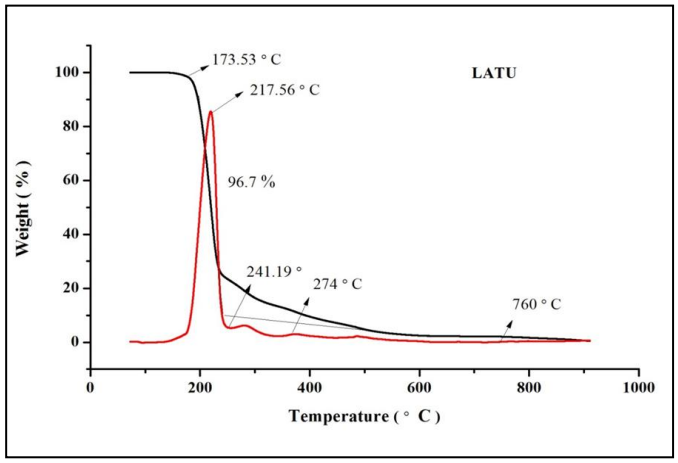

Figure 11 TGA and DTA curves of LATU crystal

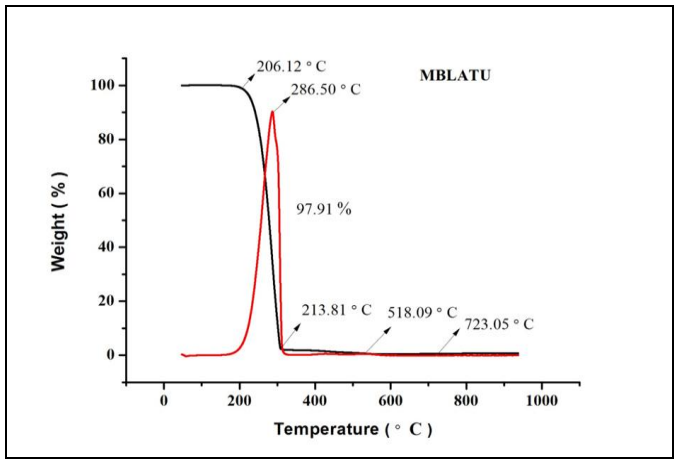

Figure 12 TGA and DTA curves of MBLATU crystal

The powder samples were used for the analysis in the temperature range of 0 ˚C to 1000˚C at a heating rate of 10˚C/min in the nitrogen atmosphere. In pure LATU, the major weight loss occurs between 173.53 ˚C and 241.19 ˚C.

The change in weight loss confirms the decomposition nature of the sample. Differential thermal analysis confirms through a sharp endothermic peak at 217.56˚C revealing the major weight loss. Further, degradation of the sample takes place from 274 ˚C to 760 ˚C where the loss of weight is about 5.41% due to liberation of volatile substances like sulfur oxide and amino acid L-Alanine [21]. The weight loss of 2.976 % at the end is due to the release of CO molecules. Hence, it is concluded that the grown material is thermally stable up to 173.53˚C. In methylene blue dye admixtured LATU crystal, the major weight loss occurs between 206.12 ˚C and 213.81 ˚C. The change in weight loss confirms the decomposition nature of the sample. Differential thermal analysis confirms through a sharp endothermic peak at 286.50˚C revealing the major weight loss. Further, degradation of the sample takes place from 213.81 ˚C to 518.09 ˚C where the loss of weight is about 2.38 % due to absorption of energy for breaking of bonds during the decomposition of the compound. Hence, it is concluded that the methylene blue dye admixtured LATU crystal is suitable for optoelectronics applications up to 206.12 ˚C.

Dielectric Analysis

The dielectric studies of pure LATU and methylene blue dye admixtured LATU crystals were carried out using the HIOKI 3532-50 LCR HITESTER instrument. The capacitance values for LATU and MBLATU crystals were determined for frequencies varying from 50 Hz to 5 MHz at room temperature. The variations of dielectric constant and dielectric loss as a function of log frequency are shown in **figure 13** and **figure 14**.

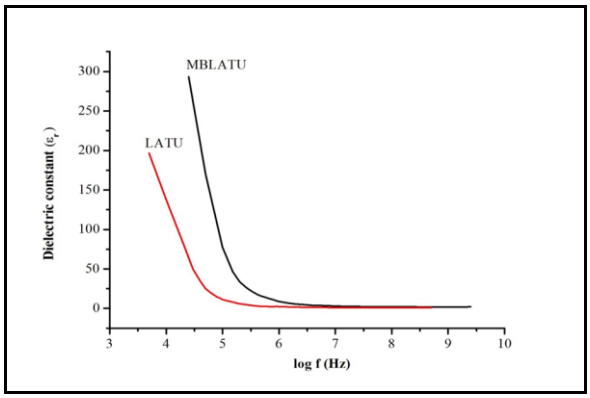

Figure 13 Variation of dielectric constant of pure LATU and MBLATU

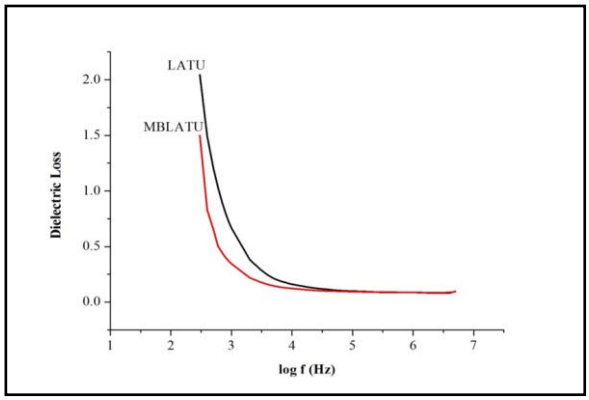

Figure 14 Variation of dielectric loss of pure LATU and MBLATU

It is observed that the dielectric constant of pure LATU is 196 where 293 for methylene blue dye admixtured LATU crystal. The high value of dielectric constant at low frequencies may be due to incorporation of methylene blue dye in LATU in the grown crystal and better orientation of dipoles in the molecules of the crystals. The low value of dielectric loss indicates that the pure and methylene blue dye admixtured LATU crystals have lesser defects, which is a desirable property for NLO applications.

Microhardness Measurements

Microhardness behaviour of pure LATU and MBLATU single crystals were tested by using Shimadzu make-model-HMV-2 fitted with Vickers pyramidal indenter and attached to an incident light microscope. The indentations were made on the flat surface with the load ranging from 25 to 100 g and the indentation time was kept as 10s for all the loads. The Vickers hardness number Hv was calculated from the following expression,

$$\mathbf{H_V = ((1.8544*P)) / d^2 \quad kg / mm^2} \qquad (2)$$

where P is the applied load in kg, d is the diagonal length of the indentation impression in mm and 1.8544 is a constant of a geometrical factor for the diamond pyramid. Vickers hardness number was calculated and a graph has been plotted between the hardness values and the corresponding loads for the crystals as shown in **figure 15**.

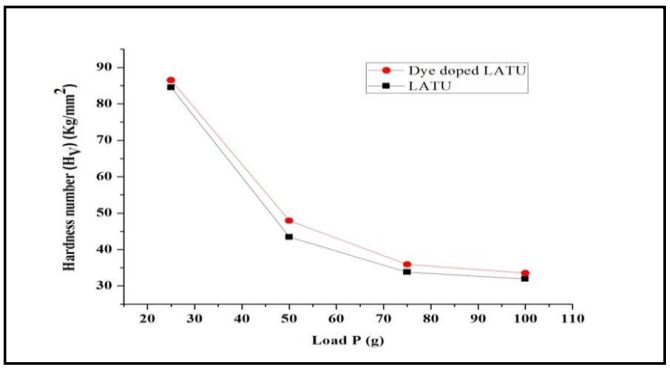

Figure 15 Variation of hardness with applied load for LATU and MBLATU single crystals

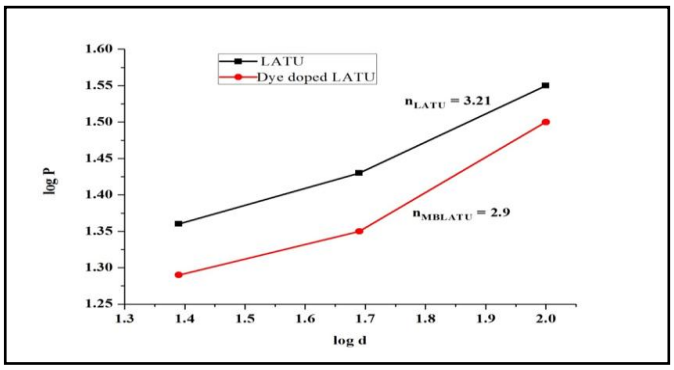

Figure 16 Variation of log (P) with log (d) for LATU and MBLATU single crystals

From the results, it is observed that the hardness number decreases with increasing load up to 75 g and attains saturation for further increase in load. Beyond this load cracks were found both in pure LATU and MBLATU single crystals. From the **figure 15**, it is observed that the microhardness value of dye admixtured crystal is slightly higher than that of the pure LATU and it is due to the presence of organic methylene blue dye molecule in the interstitial sites of pure LATU crystal. The Mayer's index number was calculated from the Mayer's law, which relates the applied load(P) and indentation diagonal length(d).

$$\mathbf{P = a * d^n} \qquad (3)$$

where 'a' is the material constant and 'n' is the Mayer's index or work hardening coefficient. The values of the work hardening coefficient (n) were estimated from the plot of log P versus log d drawn by the least square fit method and it is shown in **figure 16**. The work hardening coefficients (n) for pure LATU and methylene blue dye admixtured LATU crystals were found to be 3.21 and 2.9 respectively. Onitsch [22] pointed out that 'n' lies between 1 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials. The observed values of Mayer's index for LATU and MBLATU are 3.21 and 2.9 and hence they belong to the soft materials category.

NLO Studies

Nonlinear optical (NLO) property of pure L-Alanine Thiourea (LATU) and methylene blue dye admixtured LATU crystals were determined by Kurtz powder technique using the Nd:YAG Q-switched laser beam. The samples of same sizes were illuminated using Q-switched, mode locked Nd:YAG laser with input pulse of 6.2 mJ. The second harmonic signals of 384 mV and 430 mV were obtained for pure and methylene blue dye admixtured LATU crystals with reference to KDP (275 mV). Thus, the SHG efficiency of LATU and methylene blue dye admixtured LATU crystals was found to be 1.39 and 1.56 times greater than the standard KDP crystal. The addition of methylene blue dye in LATU crystal increases the SHG efficiency 1.56 times greater than KDP crystal efficiency.

Conclusion

Good quality of LATU and methylene blue dye admixtured LATU crystals were grown by slow evaporation method. The unit cell parameters of the crystals obtained from single crystal XRD showed that the LATU and MBLATU crystals belong to monoclinic system with space group $P2_1$. Sharp peaks of powder XRD pattern of the crystals

confirm the good crystalline nature of the grown crystals and the incorporation of methylene blue dye into LATU crystal lattice. From the HRXRD studies, it is clearly demonstrated that the crystalline perfection of grown crystals and the presence of dye in LATU crystal sites. The functional groups of MBLATU crystal were identified by FTIR spectral analysis and they have confirmed the presence of organic additive methylene blue dye in LATU crystal. The UV-vis-NIR transmittance spectra showed that the crystals had a wide optical window and the absorption due to methylene blue dye in LATU crystal. From the optical absorption studies, the value of band gap was determined as 5.2 eV for LATU and 4.4 eV for MBLATU crystals. The addition of methylene blue dye in LATU crystal increased the thermal stability of pure LATU crystal. The sharpness of the endothermic peak shows good degree of crystallinity of the crystal. The Vickers micro hardness values were calculated in order to understand the mechanical stability of the crystals. Dielectric studies for the crystal were studied. NLO studies have confirmed that the SHG efficiency value was significantly enhanced due to the presence of methylene blue dye in LATU crystal.

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