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RESEARCH ARTICLE

A STUDY ON THE GROWTH, OPTICAL, THERMAL, DIELECTRIC, LASER DAMAGE THRESHOLD AND MECHANICAL PROPERTIES OF AMARANTH DYE DOPED THIOUREA SINGLE CRYSTALS

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ABSTRACT

Pure and 2 mol% Amaranth dye doped L-Alanine Thiourea (LATU) crystals were grown by slow evaporation technique. The cell parameters and crystallinity of pure and dye admixtured LATU crystals were confirmed by single crystal X-ray diffraction, powder crystal X-ray diffraction and high resolution X-ray diffraction analyses. The doping of the Amaranth dye in the grown crystal has been confirmed qualitatively by the FTIR spectroscopy. The optical transparency of the crystals was identified from the UV-vis-NIR transmission spectrum. The laser damage threshold value significantly enhanced for Amaranth dye admixtured LATU crystal in comparison with pure LATU crystal. Thermo Gravimetric Analysis shows that the thermal stability of the crystal increases with dopant concentration. The crystals were further subjected to other important characterizations such as dielectric measurement, micro hardness and NLO studies. The improvement in Second Harmonic Generation efficiency of doped crystal has also been reported.

INTRODUCTION

NLO materials in their single crystal form have wide applications in high-energy lasers for inertial confinement fusion research (Nicoud and Twieg, 1987), colour display, electro-optic switches, frequency conversion etc., (Delfino, 1979). Hence, there is a great demand to synthesize new NLO materials and grow their single crystals. In parallel to the invention of new NLO materials, it is also important to modify the physical, optical and electrical properties of these materials either by adding functional groups (Bernal and Kristallogr, 1931) or incorporation of dopants (Simpson and Marsh, 1966; Destro *et al.,* 1988) for tailor made applications. In the presence of dopants growth promoting factors like growth rate (Zaitseva and Carman, 2001) and many of the useful physical properties like optical transparency (Angeli Mary and Dhanuskodi, 2001; Hellwege and Hellwege, 1982) second harmonic generation (SHG) efficiency (Destro *et al.,* 1988), laser damage threshold (LDT) etc. get enhance. The dopants or additives also influence the crystalline perfection which may in turn influence the physical properties depending on the degree of doping and as per the accommodating capability of the host crystal (Alfred Cecil Raj, 2013). Among organic crystals for nonlinear optics (NLO) applications, amino acids display specific features of interest (Nalini Jayanthi *et al.,* 2013), such as molecular chirality which secures acentric crystallographic structures, absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions and zwitterionic nature of the molecule, which favours crystal hardness. Further to that, amino acids can be used as chiral auxiliaries for nitro-aromatics and other donor-acceptor molecules with large hyperpolarizability (Velikhov, 2007). The growth of large single crystals of amino acids has been little investigated so far, even as regards the simplest acentric member of the family, L-Alanine (CH_3CHNH_2COOH). L-Alanine was first crystallized by BERNAL and later by SIMPSON *et al.* and DESTRO *et al.*, who refined the structure (a = 6.032 Å, b = 12.343 Å, c = 5.784 Å; $\alpha = \beta = \gamma = 90°$) and assigned it the $P2_12_12_1$ space group (12-14). In both cases, very small crystals were grown, unsuitable for optical investigations. In the recent years, complex of thiourea NLO crystals have attracted among the researchers (Lal and Bhagavannarayana, 1989) due to its flexibility in synthesis of a new complex. Thiourea ligand has both S and N donors; it can be coordinated either through S or N with few amino acid and forms a stable organic complex. Thiourea is an organic matrix modifier due to its large dipole moment and its ability to form hydrogen bonds (Batterman and Cole, 1964). A Thiourea crystal finds widespread use as frequency doublers in laser applications and was studied in great detail. Improvement in the quality of the Thiourea crystals and the performance of this crystal-based device can be realized with suitable dopants. To analyse the influence of dye based dopant on the centro symmetric Thiourea molecule, when combined with amino acids yields non-centrosymmetric complexes, which possess in

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general good nonlinear optical properties (Bhagavannarayana *et al.,* 2010). Some of the nonlinear crystals of the amino acid complexes of Thiourea reported are glycine Thiourea (Bhagavannarayana and Kushwaha, 2010), L-Histidine Thiourea (Anandan *et al.,* 2012), L-Alanine Thiourea (Ramajothi and Dhanuskodi, 2007), Methylene blue admixtured L-Alanine Thiourea (Dhumane *et al.,* 2010) and Rhodamine dye admixtured L-Alanine Thiourea (Onitsch, 1956). Among these the second harmonic generation efficiency (SHG) of glycine Thiourea crystal was 0.5 times that of KDP crystal, the SHG efficiency of L-Histidine Thiourea crystal 4.1 times that of KDP crystal, the SHG efficiency of L-Alanine Thiourea crystal 1.4, Methylene blue admixtured L-Alanine Thiourea crystal 1.56 times that of KDP crystal and Rhodamine dyeadmixtured L-Alanine Thiourea crystal 2.04 times that of KDP crystal. Amaranth dye is a synthetic acid dye containing both NN and CC chromophore groups (pyrazolone dye). It was made from amaranth plants. It is a red-brown dye; soluble in water; decomposes at 120˚C without melting; has been used in colouring food and in cosmetics. Thisanionic dye, which is stable and water soluble with an absorption peak at 520 nm, was chosen as a representative species for this study. To the best of our knowledge, there are no reports available on the influence of Amaranth dye on the growth and physical properties of L-Alanine Thiourea single crystals.

Experimental Procedure

L-Alanine Thiourea (LATU) was synthesized by dissolving high purity Thiourea and L-Alanine in theequimolar 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.

$$H_2N - CS - NH_2 + CH_3CHNH_2\,COOH\ H_2N - CS - NH_3{}^{-}CH_3CHNH_2COO^{+}$$

(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 (Palanisamy and Balasundaram, 2008). 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 Amaranthdye (2mol%) admixtured LATU salt. 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 LATU and Amarnathdye admixtured LATU (AMLATU) crystals are shown in Fig. 1 and Fig. 2.

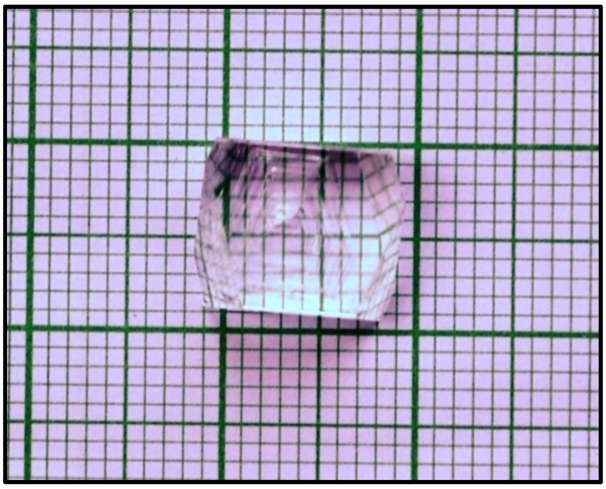

Fig. 1. Grown LATU crystal

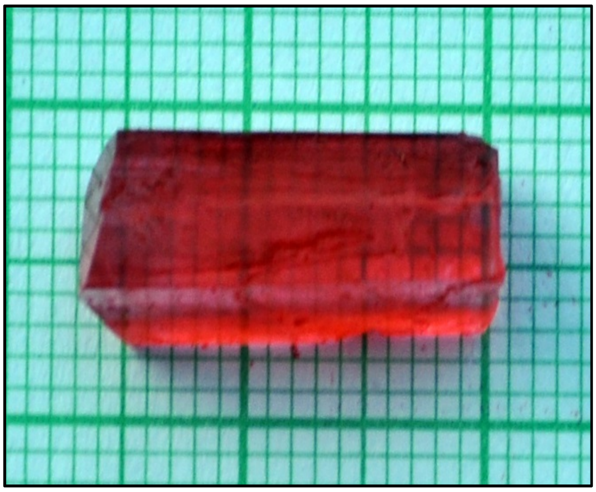

Fig. 2. Grown AMLATU crystal

RESULTS AND DISCUSSION

Single crystal XRD analysis

The single crystal XRD analysis of LATU and Amaranth dye admixtured LATU(AMLATU) 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 AMLATU crystals obtained from single crystal XRD analysis arepresented in Table 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 Amaranth dye 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 AMLATU were crushed into fine powder and powder X-ray diffraction analysis has been carried out using Rich Seifert X-ray diffractometer Table 2. Miller indices, d-spacing and 2θ-values of L-Alanine Thiourea (LATU) single crystaldetermined from powder XRD analysis using RexCell software.

Table 1. Comparison of lattice parameters of LATU and AMLATU

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.	AMLATU	a = 9.6811 Å b = 5.6251 Å c = 9.4011 Å	α= γ =90° β =109.48°	511.96 $Å^3$	Monoclinic	$P2_1$

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

S. No.	h	k	l	d(obs) (A°)	d(calc) (A°)	2θ (obs) (deg)	2θ (calc) (deg)
1	1	0	0	4.58479	4.58331	19.337	19.343
2	0	1	0	4.43740	4.44123	19.986	19.968
3	0	0	2	4.27836	4.28026	20.737	20.727
4	0	1	-2	3.81086	3.81282	23.314	23.302
5	0	1	1	3.48218	3.47963	25.550	25.569
6	2	0	-3	3.13881	3.13886	28.401	28.401
7	1	-1	-2	3.07372	3.07378	29.015	29.015
8	1	-1	1	2.93698	2.93576	30.398	30.411
9	2	1	-3	2.84657	2.84696	31.388	31.384
10	2	0	-1	2.73649	2.73706	32.685	32.678
11	1	-1	-3	2.52323	2.52354	35.536	35.532
12	2	1	-5	2.46934	2.46885	36.338	36.346
13	1	2	-2	2.31055	2.31040	38.933	38.935

Table 3. Miller indices, d-spacing and 2θ-values of Amaranth dye admixture LATU (AMLATU) single crystal determined from powder XRD analysis using RexCell software

S. No.	h	k	l	d(obs) (A°)	d(calc) (A°)	2θ (obs) (deg)	2θ (calc) (deg)
1	1	1	1	4.58479	4.58976	19.337	19.316
2	2	0	-1	4.43740	4.43163	19.986	20.012
3	0	2	0	4.27487	4.27224	20.754	20.767
4	0	0	2	3.81086	3.80861	23.314	23.328
5	0	1	2	3.48218	3.47868	25.550	25.576
6	3	0	-1	3.14621	3.14441	28.333	28.349
7	2	1	-2	3.08081	3.07879	28.947	28.967
8	3	1	-1	2.94668	2.95093	30.296	30.251
9	0	2	2	2.84657	2.84293	31.388	31.429
10	3	0	1	2.73649	2.73578	32.685	32.694
11	1	3	1	2.52323	2.52339	35.536	35.534
12	1	1	-3	2.46934	2.47157	36.338	36.304
13	4	1	-1	2.31055	2.31056	38.933	38.933

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 AMLATU are shown in Table 2 and Table 3 with the help of RexCell program and their powder diffractograms are shown in Fig. 3 & Fig. 4.

From the X-ray powder diffraction data, the lattice parameters for AMLATU were found to be a = 9.6711 Å, b = 5.6391 Å and c = 9.4199 Å. This is in close agreement with the values obtained from single crystal X-ray diffraction analysis for AMLATU. The change in intensity of peaks as well as addition in number of peaks for AMLATU in the powder X-ray diffraction pattern reveal that the dye doped crystal is slightly distorted compared to the pure LATU. This may be attributed to strains on the lattice by the absorption or substitution of Amaranth dye in LATU 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 $MoK\alpha_1$ 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 $MoK\alpha_1$ 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.

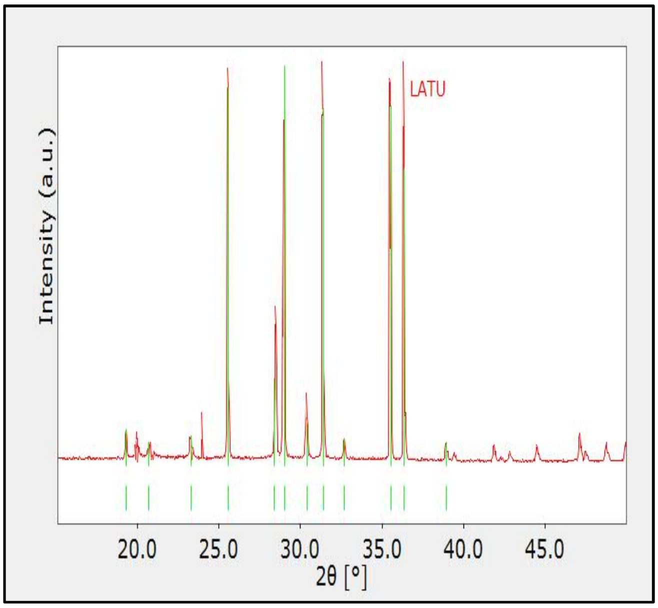

Fig.3. PWXRD spectrum of LATU crystal

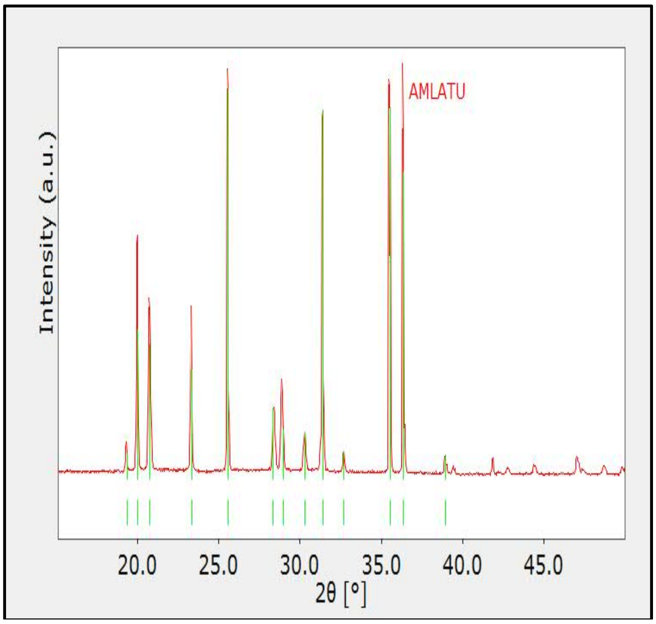

Fig. 4. PWXRD spectrum of AMLATU crystal

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 Amaranth dye admixtured LATU crystals were first lapped and chemically etched in a non-referential etchant of water and acetone mixture in 1:2 ratios. Fig. 5 and Fig. 6 show the high-resolution diffraction curves (DCs) recorded for pure LATU and Amaranth dye admixtured LATU crystals using (3 0 0) diffracting planes in symmetrical Bragg geometry by employing the multicrystal X-ray diffractometer with $MoK\alpha_1$ radiation.

The curves are very sharp having full width at half maximum (FWHM) of 14 arc sec for pure LATU and 37 arc sec for Amaranth dye admixtured LATU crystals as expected for nearly perfect crystals from the plane wave dynamical theory of X-ray diffraction (Batterman and Cole, 1964). 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.

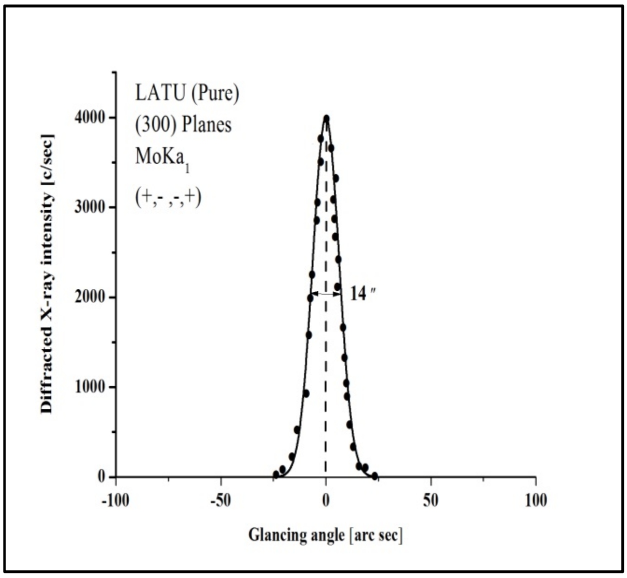

Fig. 5.HRXRD curve of pure LATU crystal

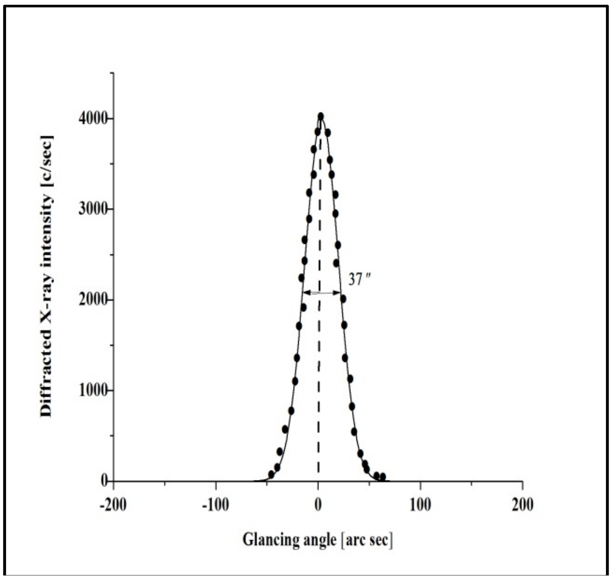

Fig. 6. HRXRD curve of AMLATU crystal

The increase in FWHM without having any additional peaks in DC of Amaranth dye doped LATU crystal indicates the incorporation of Amaranth dye in the crystalline matrix of LATU crystal. In DC of Amaranth 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 Amaranth 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) intensityat slightly higher Bragg angles(θ_B) as d and sin θ_B are inversely proportional to each other in the Bragg equation (2d sin θ_B = nλ; 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 (Bhagavannarayana *et al.,* 2010). The HRXRD results confirm an important finding that Amaranth 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 (Bhagavannarayana and Kushwaha, 2010).

Fourier Transform Infrared Spectroscopy

The mid Fourier transform infrared spectrum of pure and dye doped LATU crystals were recorded at 300 K in the range of 4000–400 cm^{-1} using the KBr pellet technique. The FTIR spectra of pure and dye admixtured LATU crystals are shown in Fig. 7 and Fig. 8.

The incorporation of Amaranth dye in LATU crystal has been strongly verified by spectral analysis. The absorptions at3796, 3560 and 3373cm^{-1}in the Amarnath dye doped LATU crystals may be attributed to hydrogen bonded OH stretching. The NH^{+3} asymmetric bending and CH_2 stretching vibrations occur at 3181 cm^{-1} and at 2809 cm^{-1}. The asymmetric stretching vibration of $CO_2$is observed at 1558 cm^{-1}. In the Amaranth dye LATU spectrum, the OH stretching in the high energy region is very much broadened, due to hydrogen bonding. The peak at 511$cm^{-1}$is due to C=S stretching vibration.

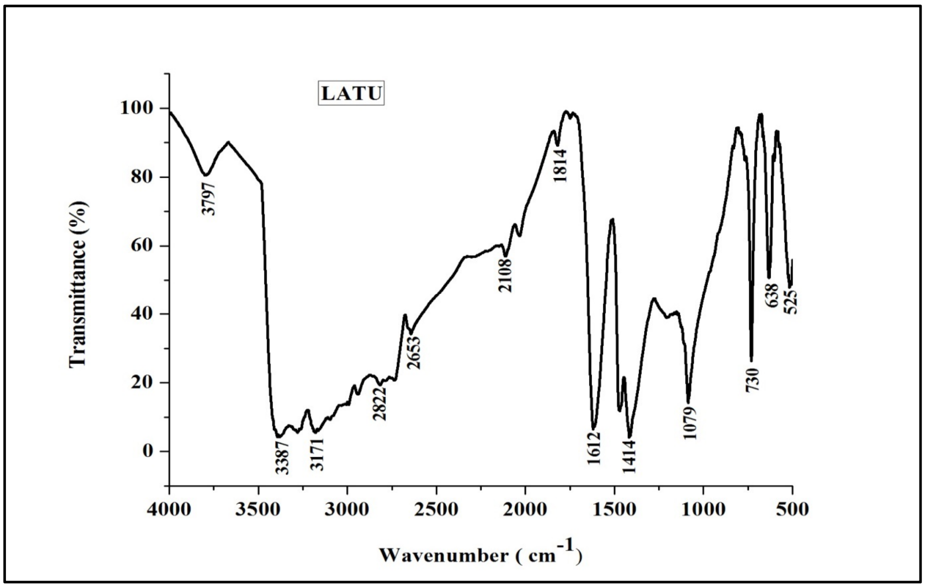

Fig. 7. FTIR spectrum of grown L-Alanine Thiourea (LATU) single crystal

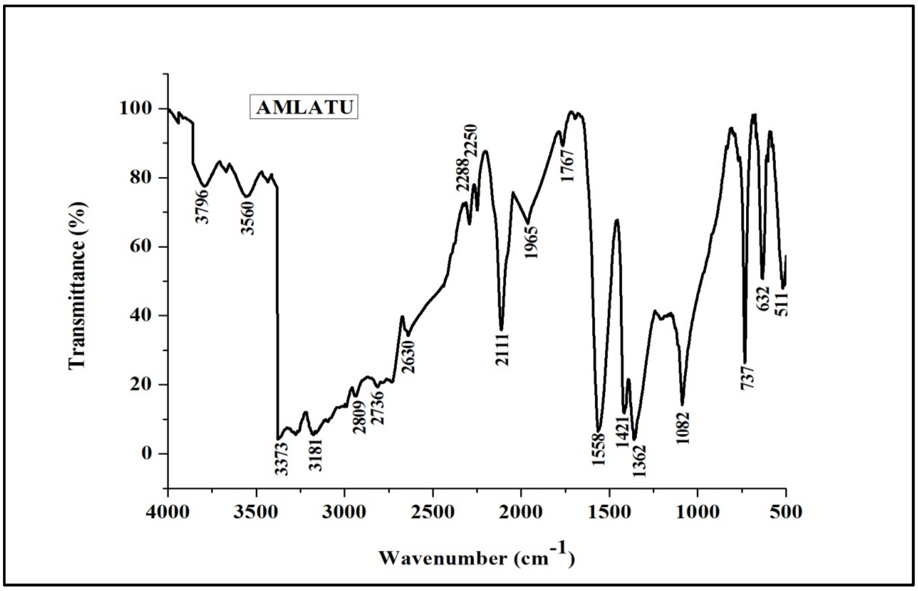

Fig. 8. FTIR spectrum of grown Amaranth dye admixtured LATU (AMLATU) single crystal

The aliphatic C-H stretching mode at 2736cm^{-1}confirms the presence of Amaranth dye in LATU. The narrow bands at 737, 632 and 511 cm^{-1}are observed in Amaranth dye added as compared to LATU. The vibration frequencies of L-Alanine Thiourea are compared with Amaranth dye admixtured L-Alanine Thiourea in Table 4 to confirm the incorporation of Amaranth dye in LATU crystal.

Optical band gap energy (E_g) calculation

The band gap energy of the pure and Amaranth dye admixtured LATU crystals were calculated from the Fig. 10 by taking Photon energy (hυ) values along X-axis and $(\alpha h\upsilon)^2$ values along Y-axis for LATU and AMLATU crystals. The optical absorption coefficient (α) was calculated using the relation

Table 4. Infrared absorption frequencies (cm^{-1}) of L-Alanine Thiourea (LATU) and Amaranth dye admixtured LATU (AMLATU) crystals

S.No.	L-Alanine Thiourea(LATU)	Amaranth dye admixtured LATU(AMLATU)	Assignment
1	3797	3796, 3560, 3373	OH-stretching
2	3171	3181	NH_3^+ symmetric stretching
3	2822	2809	$=CH_2$ stretching
4	-	2736	Aliphatic (C-H) stretch
5	2653	2630	C-H symmetric stretching
6	2108	2111	Over tone region with a combination of symmetric NH_3^+ bending and torsional vibrations
7	1814	1965	C=O absorption
8	1612	1767	Asymmetric bending of NH^{+3} and C=N stretching
9	-	1558	CO_2asymmetric stretching
10	1414	1421	C= O stretching
11	1079	1082	Symmetrical C-O-C stretching
12	730	632	C-H in plane bending
13	638	511	C=S stretching

UV-visible spectral study

The UV-visible spectra of pure and Amaranth 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 (Anandan *et al.,* 2012). The UV-vis spectra of LATU and AMLATU are shown in Fig. 9. In the case of pure LATU, a sharp fall in percent transmittance is occurred at 209 nm. For AM dye admixtured LATU, the fall in percent transmittance is occurred at 385.93 nm. Such variation in percent transmittance is due to electronic excitation of AM dye doped LATU crystal. The good transparency with lower cut off wavelength at 385.93 nm makes the AMLATU crystal useful for optoelectronics applications.

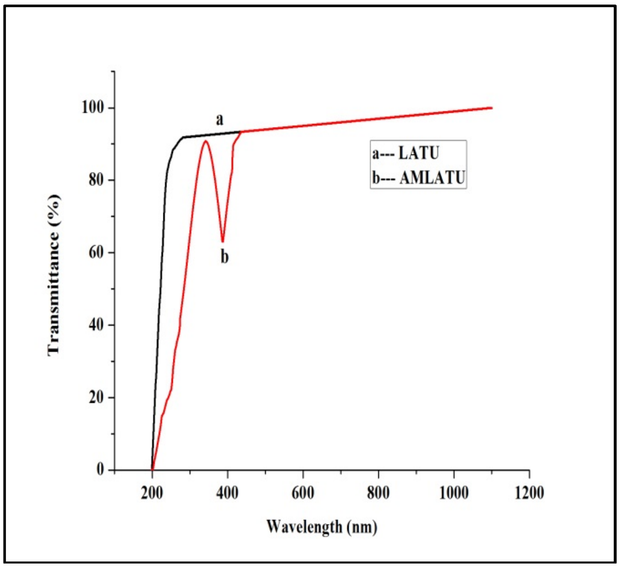

Fig. 9. UV-vis-NIR absorption spectra for LATU and AMLATU crystals

$$\alpha = (2.3026 * \log (1/T)) / t \quad \text{……..(1)}$$

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 AMLATU and found to be 5.2eV and 4.8eV 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 AMLATU 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 (Ramajothi and Dhanuskodi, 2007).

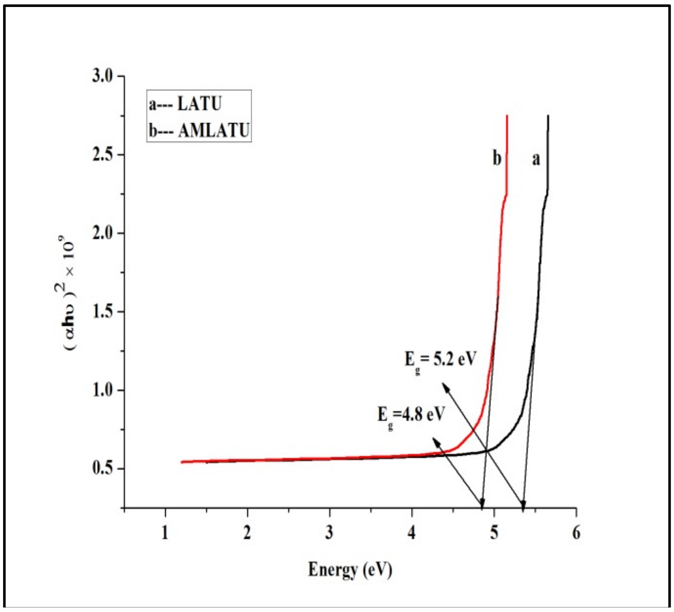

Fig. 10. Photon energy vs $(\alpha h\upsilon)^2$ for LATU and AMLATU crystals

Thermo Gravimetric Analysis (TGA)

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out for LATU and AMLATU crystals using TA Q-500 analyser. TGA and DTA curves for pure and Amaranth dye admixtured LATU are shown in Fig. 11 and Fig. 12. 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 (Dhumane *et al.,* 2010). 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.

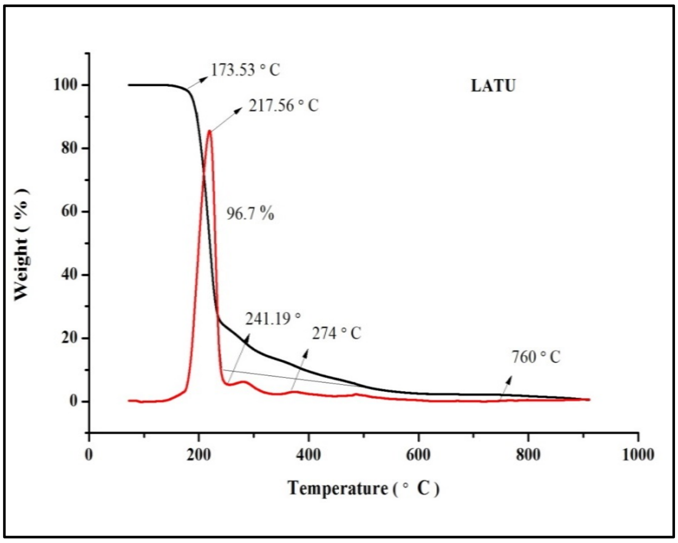

Fig. 11. TGA and DTA curves of LATU

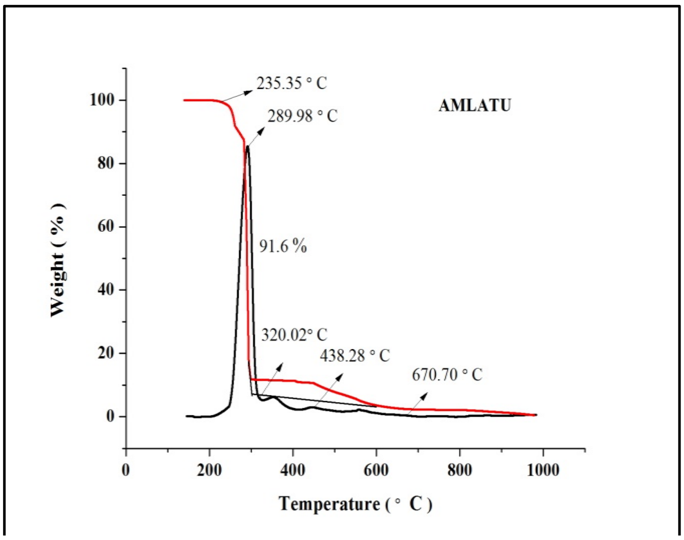

Fig. 12. TGA and DTA curves of AMLATU crystalcrystal

In Amaranth dye admixtured LATU crystal, the major weight loss occurs between 235.35 ˚C and 320.02 ˚C. The change in weight loss confirms the decomposition nature of the sample. Differential thermal analysis confirms through a sharp endothermic peak at 289.98 ˚C revealing the major weight loss. Further, degradation of the sample takes place from 438.28 ˚C to 670.70 ˚C where the loss of weight is about 2.01 % due to absorption of energy for breaking of bonds during the decomposition of the compound. Hence, it is concluded that the Amaranth dye admixtured LATU crystal is suitable for optoelectronics applications up to 235.35˚C.

Dielectric Analysis

The dielectric studies of pure LATU and Amaranth dye admixtured LATU crystals were carried out using the HIOKI 3532-50 LCR HITESTER instrument. The capacitance values for LATU and AMLATU 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 Fig. 13 and Fig. 14.

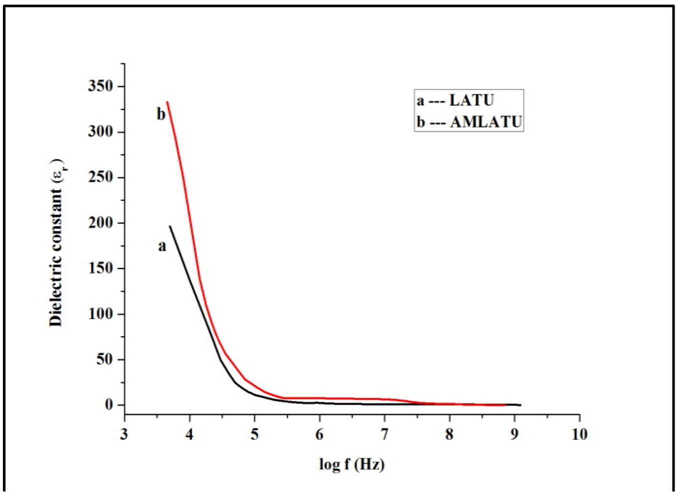

Fig. 13.Variation of dielectric constant of pure LATU and AMLATU

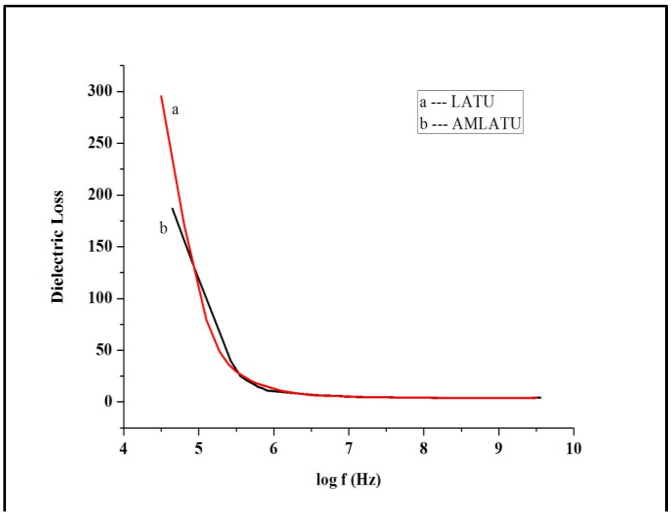

Fig. 14. Variation of dielectric loss of pure LATU and AMLATU

It is observed that the dielectric constant of pure LATU is 196 where 333 for Amaranth dye admixtured LATU crystal. The high value of dielectric constant at low frequencies may be due to incorporation of Amaranth 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 Amaranth dye admixtured LATU crystals have lesser defects, which is a desirable property for NLO applications.

Microhardness Measurements

Microhardness behaviour of pure LATUand AMLATU 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 H_v was calculated from the following expression,

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

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 Fig. 15. 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 AMLATU single crystals. From the Fig. 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 Amaranth dye molecule in the interstitial sites of pure LATU crystal.

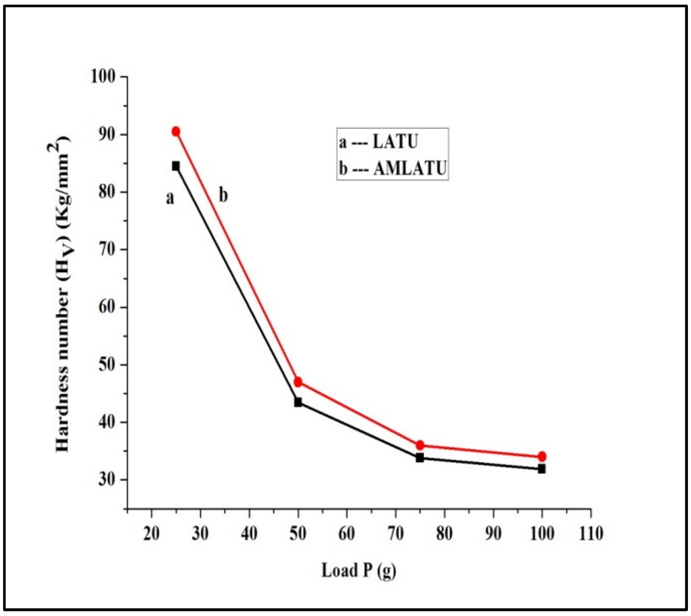

Fig. 15.Variation of hardness with applied load for LATU and AMLATU single crystals

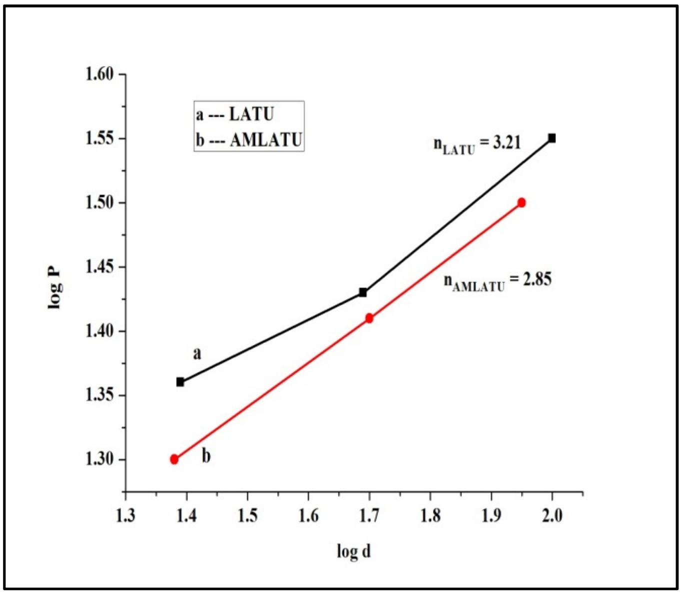

Fig. 16. Variation of log (P) with log (d) for LATU and AMLATU single crystals

The Mayer's index number was calculated from the Mayer's law, which relates the applied load(P) and indentation diagonal length(d).

$$P = ad^n \qquad \text{..........(3)}$$

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 Fig. 16.The work hardening coefficients (n) for pure LATU and Amaranth dye admixtured LATU crystals were found to be 3.21 and 2.85 respectively. Onitsch (1956) 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 AMLATU are 3.21 and 2.85 and hence they belong to the soft materials category.

Laser damage threshold studies

The laser damage density is one of the important parameters that decide the applicability of the material for high power laser applications. The laser damage threshold values were measured using a Q-switched Nd-YAG laser source of pulse width 10ns and 10Hz repetition rate operating in TEM00 mode. The energy per pulse of 532nm laser radiation attenuated using appropriate neutral density filters was measured using an energy meter (Coherent EPM 200) which is externally triggered by the Nd:YAG laser. If the material has a low damage threshold, it severely limits its application, though it may have excellent properties like high optical transmittance and high SHG efficiency (Onitsch *et al.,* 1956). For surface damage, the sample was placed at the focus of a plano-convex lens of focal length 30 cm. The (100) plane of pure and dye admixtured crystals was used for the laser damage studies. The surface threshold of the crystal was calculated using the expression:

Power density (Pd) = E/ $\tau\pi r^2$ ....(4)

Where E is the energy (mJ), τ is the pulse width(ns) and r is the radius of the spot (mm). The measured multiple shot (150 pulses) laser damage threshold values of pure and dye admixtured LATU crystals are 9 and 8.1 GW/cm^2 respectively. The decrease in laser damage threshold value of dye admixtured LATU may be due to incorporation of dye in the LATU crystals

NLO Studies

Nonlinear optical (NLO) property of pure L-Alanine Thiourea (LATU) and Amaranth 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 690 mV were obtained for pure and Amaranth dye admixtured LATU crystals with reference to KDP (275 mV). Thus, the SHG efficiency of LATU and Amaranth dye admixtured LATU crystals was found to be 1.39 and 2.5 times greater than the standard KDP crystal. The relative SHG efficiency of Amaranth admixtured LATU crystal was found to be 1.79 times higher than that of pure LATU crystal.

Conclusion

Good quality of LATU and Amaranth 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 AMLATU 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 Amaranth dye into LATU crystal lattice. The functional groups of AMLATU crystal were identified by FTIR spectral analysis and they have confirmed the presence of organic additive Amaranth dye in LATU crystal. The UV-vis-NIR transmittance spectra showed that the crystals had a wide optical window and the absorption due to Amaranth dye in LATU crystal.

The addition of Amaranth 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 Amaranth dye in LATU crystal.

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