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RESEARCH ARTICLE

GROWTH AND CHARACTERIZATION OF PURE AND CRYSTAL VIOLET DYE ADMIXTURED L-ALANINE THIOUREA SINGLE CRYSTALS

***Kannan, R., Jayaraman, D. and Aravindhan, S.**

Department of Physics, Presidency College, Chennai-600005, Tamilnadu, India

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ABSTRACT

Pure and 0.1mol% crystal violet dye doped L-Alanine Thiourea (LATU and CVLATU) 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 crystal violet 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 CVLATUcrystal in comparison with pure LATU crystal. Thermal analysis has been performed on the grown crystals. 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.

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INTRODUCTION

Many of present-day instruments and devices used in various areas of science and technology, e.g. in electronics, optics, acoustics, and lasers incorporate single crystals of various materials. Hence, growth of single crystal with single direction in a desired size and specific properties has become inevitable for further research and technology. Nonlinear optic (NLO) is a new frontier of science and technology playing a major role in the emerging era of photonics. Photonics involves the application of photons for information and image processing and is branded to be the technology of the 21st century wherein nonlinear optical processes have applications in the vital functions such as frequency shifting, optical modulation, optical logic, optical switching and optical memory (He and Liu, 1999 and Prasad and Williams, 1991). NLO materials typically have a distinct crystal structure which is anisotropic to electromagnetic radiation. Light passing through them undergoes a change in wavelength thereby releasing a photon of accumulated frequency. NLO materials can be used to double or treble the frequency of the laser light and are of considerable interest for the high speed processing of the data which is essential foroptical computing and optical telecommunication systems. The enhancement of the efficiency of the non-linear process by the appropriate choice of NLO material constitutes a central concern in all these studies. The search for suitable materials exhibiting excellent second order nonlinear optical properties has been the focus of current research activity owing to their potential applications in optoelectronics, telecommunications and optical storage devices (Bella, 2001; Marder *et al*., 1991; Wang *et al*., 1999; Cole *et al*., 2000 and Zaitseva, 2001). From materials point of view, the NLO materials can be broadly classified in three different categories such as inorganic, organic and semi-organic or metal organic materials. Inorganic and organic possess their own set of advantages and disadvantages (Blau, 1987), while in semi-organic or metal organic materials the aim is always to combine advantages of the both.In the recent past, the extensive investigations are carried out on organic materials due to their high nonlinearity compared to inorganic material. The origin of nonlinearity in the NLO material is due to the presence of delocalized π-electron system connecting donor and acceptor groups which enhance the asymmetric polarization. Recently, an extremely large number of organic compounds with non-localized π-electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities far larger than the

Corresponding author: Kannan, R.
Department of Physics, Presidency College, Chennai-600005, Tamilnadu, India.

inorganic optical materials (Zyss and Chemla, 1987). Despite of high non-linearity, the applications of organic NLO crystals have developed rather slowly because the organic molecules are constructed by weak van derwaal forces and hydrogen bonds, and it is difficultto grow large optical- quality single crystals and also, due to the often fragile nature of these crystals. The shortcoming of these crystals, such as poor physicochemical stability, low hardness and cleavage tendency and poor thermal strength obstruct their device applications. The inorganic NLO materials have some advantages like high melting point, high mechanical strength and compatible physical properties, on the other hand, such materials suffer from disadvantages like modest optical nonlinearity due to the lack of extended π-electron dislocation, absorption in the visible region, poor response time and degradative photorefractive effects, low laser damage threshold (~10 MW cm^{-2}) and poor optical transparency (Fan *et al*., 1984 and Hussaini *et al*., 2009).

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 (SwetaMoitra and TanusreeKar, 2007) or incorporation of dopants (Zernike and Midwinter, 1973; Bhagavannarayana *et al.,* 2008) for tailor made applications. In the presence of dopants growth promoting factors like growth rate (Vries *et al.,* 1998) and many of the useful physical properties like optical transparency (Kar *et al.,* 2004; Winkler *et al.,* 2000) second harmonic generation (SHG) efficiency (Bhagavannarayana *et al.,* 2008), 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.

Dye inclusion crystals are used for application of solid state lasers. The dye molecule is incorporated with the water soluble crystals and avoids many drawbacks like other solid materials such as working media for lasers. The dyes absorb in the visible range of 500–550 nm. Thus second harmonic generation of Nd-YAG laser light is suitable for pumping the dyes in order to achieve lasing effect (Raju et al., 2011). Due to broad absorption in the visible region in the dye doped crystal it can be used as a filter. Crystal Violet (CV) is one of the cationic organic dyes whose tinctorial values are very high, less than 0.1 mol% of the dye produces an obvious coloration (Pritula et al., 2009). However, there is no data in the addition of CV with LATU single crystals.The effect of crystal violet as dopant on the characteristicproperties of LATU crystal was studied by slow evaporation method. It is possible to growlarge size good quality crystals by dye method. For device fabrication we need a large size,mechanically and optically good quality single crystal. 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 general good nonlinear optical properties. This paperpresents the influence of crystal violet dye on the opticaltransmission, mechanical hardness, thermal stability, laser damage threshold, dielectric and NLO properties of L-Alanine Thiourea single crystals.

Experimental Procedure

In general, significant extension of growth rate and habit modification is possible only at low dopant concentration in the crystal growth experiments (Rajesh et al., 2010; Pritula et al., 2004). 0.1mol% crystal violet molecules are easily absorbed by the LATU surfaces due to the structural resemblance. Good quality crystals of pure and CV doped LATU crystals were grown by slow evaporation from aqueous solution. 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.

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

(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 crystal violet dye(0.1mol%) 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 Crystal Violet dye admixtured LATU (CVLATU) crystals are shown in Fig. 1 and Fig. 2.

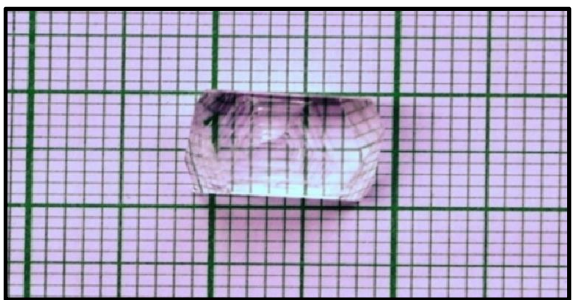

Fig. 1.Grown LATU crystal

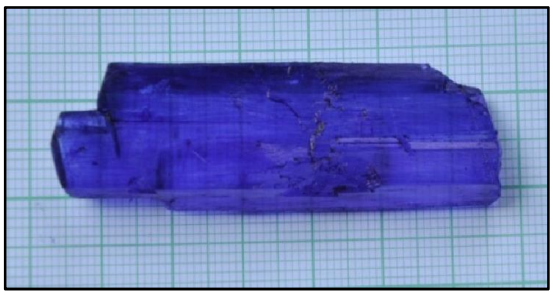

Fig. 2. Grown CVLATU crystal

RESULTS AND DISCUSSION

Single crystal XRD analysis

The single crystal diffraction analysis of LATU (pure) and CVLATU (dye doped LATU) was carried out using Enraf Nonius CAD4 single X-ray diffractometerto determine the cell parameters. From this measurement, the lattice parameters are listed in Table 1. These values agree well with the reported values the grown crystal retains its original structure. This result reveals that the crystal violet dye has entered into the lattice sites of LATU crystal.

Powder XRD Analysis

The grown pure and CV-doped LATU crystals were subjected to powder X-ray diffraction studies using a Rich Seifert X-ray diffractometer employing CuKα(1.54058 Å) radiation, scanning angle ranging from 10° to 50° at a scan rate 1°/min to confirm the crystalline phase of the grown crystal. The Miller indices (hkl), d-spacing and diffraction angle (2θ) are summarized for LATU and CVLATU crystals 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.

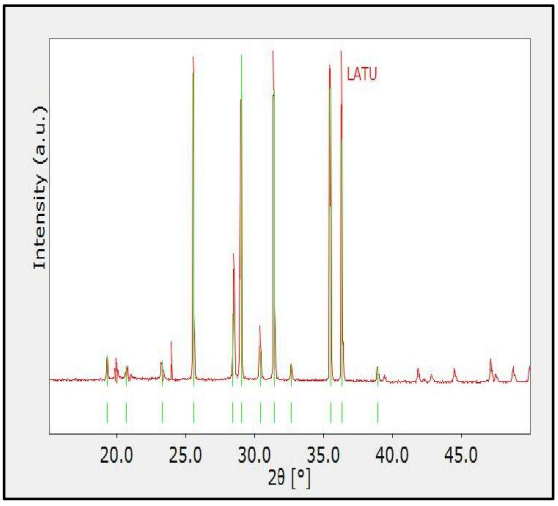

Fig. 3. PWXRD spectrum of LATU crystal

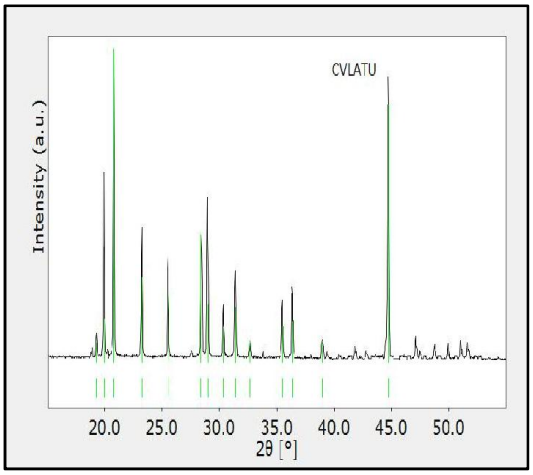

Fig. 4. PWXRD spectrum of CVLATUcrystal

From the X-ray powder diffraction data, the lattice parameters for CVLATU 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 CVLATU. The change in intensity of peaks as well as addition in number of peaks for CVLATU in the powder X-ray diffraction pattern reveal that the dye doped crystal is slightly distorted compared to the pure LATU. This may be due to the presence of CV in the LATU lattice.

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 (Lal and Bhagavannarayana, 1989) 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.

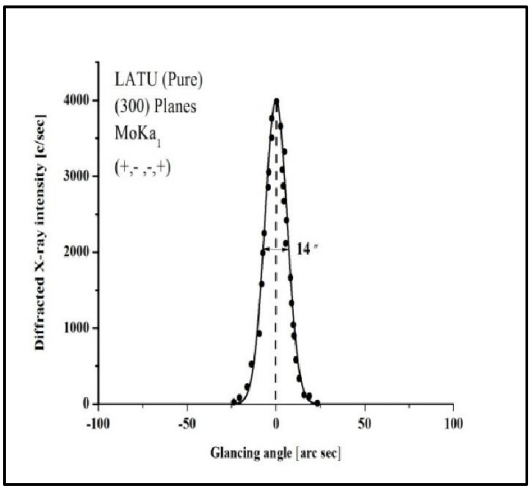

Fig. 5. HRXRD curve of pure LATU crystal

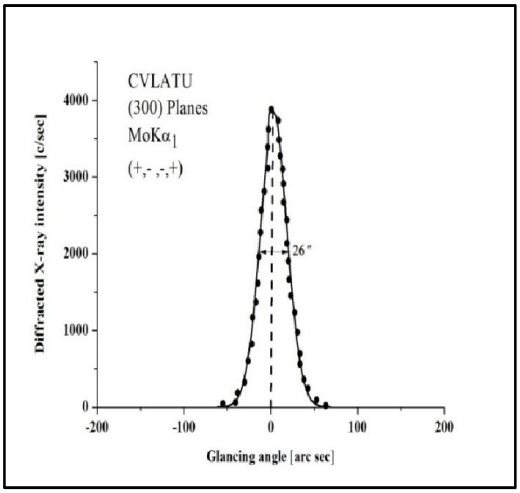

Fig. 6. HRXRD curve of CVLATU crystal

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 crystal violet 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 crystal violet 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. The curves are very sharp having full width at half maximum (FWHM) of 14 arc sec for pure LATU and 26 arc sec for crystal violet dye admixtured LATU crystals as expected for nearly perfect crystals from the plane wave dynamical theory of X-ray diffraction (Batterman et al., 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. The increase in FWHM without having any additional peaks in DC of crystal violet dye doped LATU crystal indicates the incorporation of crystal violet dye in the crystalline matrix of LATU crystal. In DC of crystal violet 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 crystal violetdopants predominantly occupy the interstitial positions in the lattice and elucidates the ability of accommodation of dopants in the crystalline matrix of the LATU crystal.

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 (Bhagavanarayana *et al.,* 2010). The HRXRD results confirm an important finding that crystal violet 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 (Bhagavanarayanaand Kushwaha, 2010).

Fourier Transform Infrared Spectroscopy

The FTIR spectrum of pure and CV dye doped LATU crystals were recorded at 300 K in the range of 4000–500 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 peak with the highest wave number 3835 cm^{-1}, 3797 cm^{-1}, 3724 cm^{-1}, 3679 cm^{-1} and 3560 cm^{-1}belongs to the asymmetric stretching vibrations of NH_3^+ in both pure and CV doped LATU crystal. The absorption peak at 2925 cm^{-1}, 2822 cm^{-1} and 2653 cm^{-1}, 2604 cm^{-1}, 2456 cm^{-1} and 2388 cm^{-1} in the pure and doped crystal is due to the hydrogen bonded OH grouping. The strongabsorption band in the region 1700-1500 $cm^{-1}$with peaks 1612 cm^{-1}1758 $cm^{-1}$is characteristic of LATU salts.

These absorptionpeaks maybe assigned to the C=N stretching and deformation vibrations NH_3^+ group. The absorption peak at 1414 cm^{-1}, 1314 cm^{-1} isdue to COO symmetric bending and stretching respectively. The next strong band at 1110 cm^{-1}, 1079 $cm^{-1}$is due to C-C-H asymmetric stretching. The presence of absorption peak at 751 cm^{-1}, 730 cm^{-1} confirms the NH wagging. The next absorption band at the low wave number region at 650 cm^{-1}, 638 cm^{-1} is assigned to COO in plane deformation.

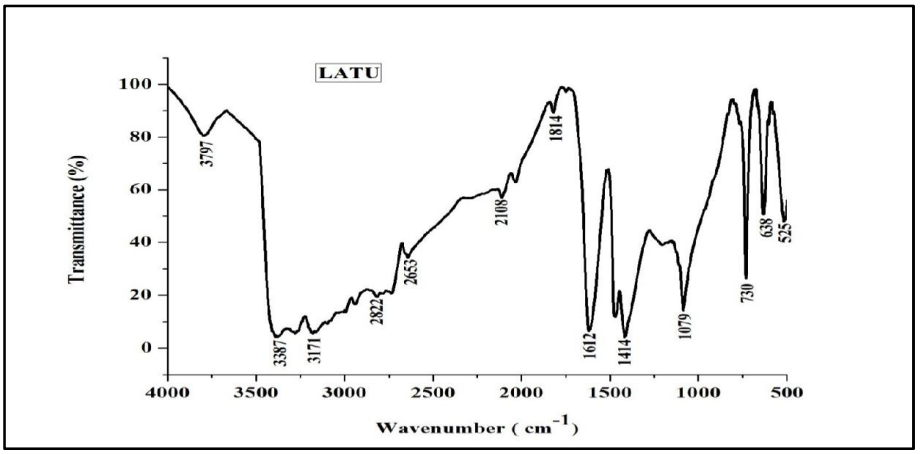

Fig. 7. FTIR spectrum of grown L-Alanine Thiourea (LATU) single crystal

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 θ_B = nλ; n and λ being the order of reflection and wavelength respectively which are fixed).

Small shifts in the vibrations are noted, this is due to the presence of dopants in the lattice of LATU. Hence the entry of dopants in the LATU lattice is clearly evident from this study.

UV-visible spectral study

The UV-visible spectra of pure and crystal violet dye admixtured analyses have been carried out using Shimadzu

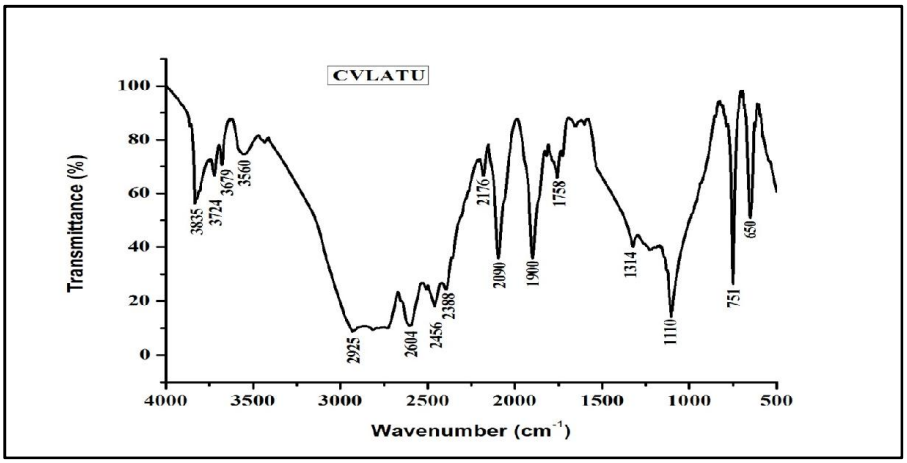

Fig. 8. FTIR spectrum of grown crystal violet dye admixtured LATU (CVLATU) single crystal.

Table 1.Comparison of lattice parameters of LATU and CVLATU

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.	CVLATU	a = 9.8011 Å b = 5.6051 Å c = 9.3911 Å	α= γ =90° β =109.48°	515.91 Å^3	Monoclinic	$P2_1$

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(calc) (A°)	2θ (obs) (deg)	2θ (calc) (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

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 CVLATU are shown in Fig. 9. In the case of pure LATU, a sharp fall in percent transmittance is occurred at 209 nm. For CV dye admixtured LATU, the fall in percent transmittance is occurred at 304.26nm. Such variation in percent transmittance is due to electronic excitation of CVdye doped LATU crystal. The good transparency with lower cut off wavelength at 304.26 nm makes the CVLATU crystal useful for optoelectronics applications.

Optical band gap energy (E_g) calculation

The band gap energy of the pure and crystal violet 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 CVLATU crystals.The optical absorption coefficient (α) was calculated using the relation

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

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 CVLATU and found to be 5.2eV and 4.9eV 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 CVLATU 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 *et al.,* 2007).

Table 3. Miller indices, d-spacing and 2θ-values of Crystal Violet dye admixtured LATU (CVLATU) 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	2	0	-2	4.58878	4.58691	19.320	19.328
2	0	1	0	4.42619	4.43214	20.037	20.010
3	1	1	0	4.25757	4.24961	20.839	20.879
4	2	1	0	3.81086	3.81316	23.314	23.300
5	2	0	2	3.47989	3.48096	25.567	25.559
6	5	0	-1	3.13512	3.13736	28.435	28.414
7	0	0	3	3.07018	3.06989	29.050	29.053
8	3	1	1	2.93698	2.93578	30.398	30.411
9	1	0	3	2.84355	2.84323	31.422	31.426
10	2	1	2	2.73649	2.73758	32.685	32.672
11	0	1	3	2.52206	2.52364	35.553	35.530
12	3	1	2	2.46710	2.46542	36.373	36.398
13	6	0	-3	2.30569	2.30522	39.018	39.026
14	6	0	-4	2.02262	2.02253	44.753	44.755

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

S.No.	L-Alanine Thiourea(LATU)	Crystal Violet dye admixtured LATU(CVLATU)	Assignment
1	3797	3835, 3724,3679, 3560	NH_3^+ asymmetric Stretching
2	2822, 2653	2925, 2604, 2456, 2388	Hydrogen bonded OH grouping
3	2108	2176	Over tone region with a combination of symmetric NH_3^+ bending and torsional vibrations
4	1814	2090, 1900	C=O absorption
5	1612	1758	NH_3^+ symmetric deformation and C=N stretching
6	1414	1314	COO^- symmetric bending and stretching
7	1079	1110	C-C-H asymmetric Stretching
8	730	751	NH wagging
9	638	650	COO^- in plane deformation

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) curve for pure and CV doped LATU crystal is shown in Fig. 11 and Fig. 12. There is no weight loss up to 173.53 ˚C and the decomposition starts at above 173.53 ˚C for pure LATU. The 96.7% of the compound decomposed between 173.53 ˚C and 241.19 ˚C. In case of CV doped LATU, there is no weight loss up to 243.57 ˚C and the decomposition starts at above 243.57 ˚C. The 97.85 % of the compound decomposed between 243.57 ˚C and 327.84 ˚C.

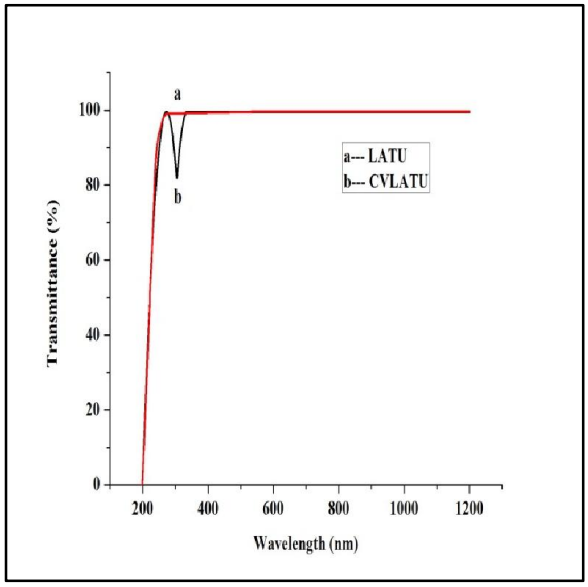

Fig. 9.UV-vis-NIR absorption spectra for LATU and CVLATU crystals

When compared to pure LATU, in the decomposition temperature difference of 70.04 ˚C has been observed in the dye doped LATU. This may be due to the presence of CV in the crystal lattice. Hence, it is concluded that the crystal violet dye doped LATU crystal is suitable for optoelectronics applications up to 243.57 ˚C.

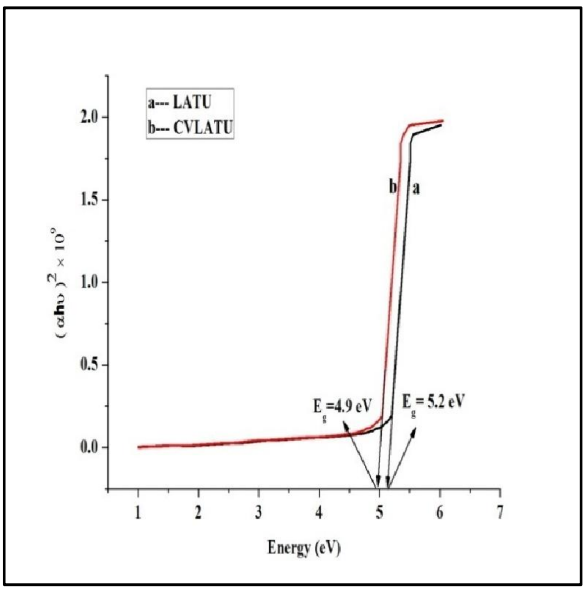

Fig. 10. Photon energy vs $(\alpha h\upsilon)^2$ for LATU and CVLATU crystals

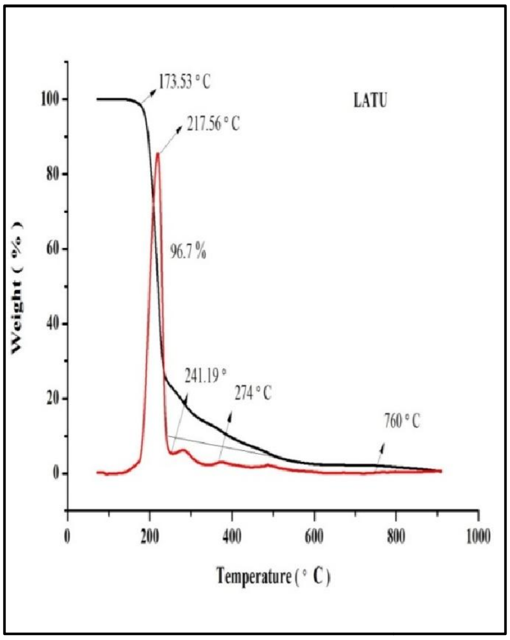

Fig. 11.TGA and DTA curves of LATU crystalcrystal

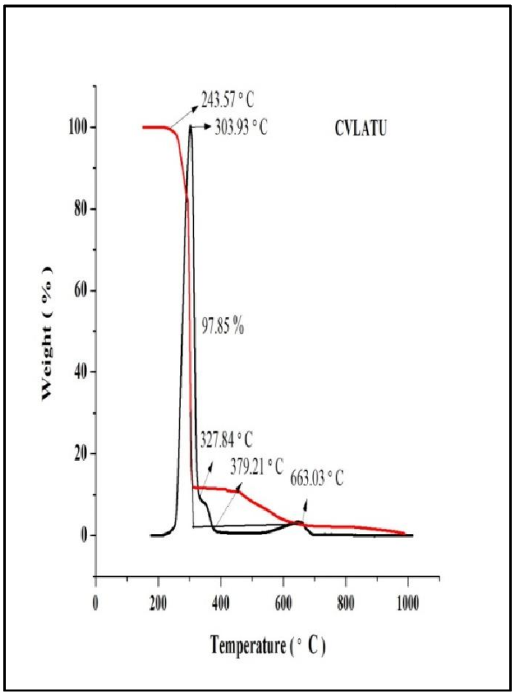

Fig. 12. TGA and DTA curves of CVLATU

Dielectric Analysis

The dielectric constant and dielectric loss of pure and dye doped LATU crystals were determined using the HIOKI 3532-50 LCR HITESTER instrument. Samples were cut to a proper thickness and polished.

Each sample was electroded on both sides with high purity silver paste so that it behaved like a parallel plate capacitor. The dielectric constant is calculated using the formula

$$\varepsilon_r = Ct/\varepsilon_o A \qquad (2)$$

where C is capacitance (F), t the thickness (m), A the area (m^2), and ε_o the absolute permittivity in the free space having a value of 8.854×10^{-12} $F \cdot m^{-1}$. The variations of dielectric constant and dielectric loss as a function of log frequency for pure and CV doped LATU crystals are shown in Fig. 13 and Fig. 14. It is observed that the dielectric constant of pure LATU is 196 where 378for crystal violet dye admixtured LATU crystal. The presence of dye increased the dielectric constant and decreased the dielectric loss due to the uniform distribution of dye molecules in the LATU crystal lattice.

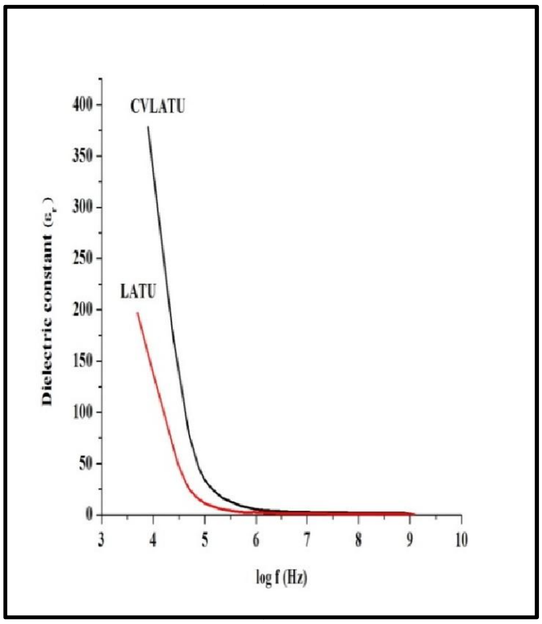

Fig. 13.Variation of dielectric constant of pure LATU and CVLATU

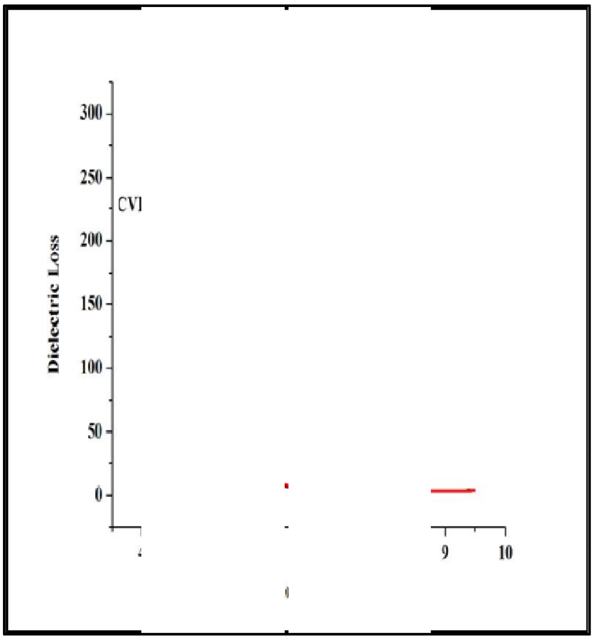

Fig. 14. Variation of dielectric loss of pure LATU and CVLATU

Microhardness Measurements

The good quality crystals are needed for various applications not only with good optical performance but also with good mechanical behaviour. Hardness of a crystal is due to the resistance offered by a solid to the movement of dislocation, practically which is caused by scratching or indentation (Rajesh et al., 2010; Dhumane et al., 2010). The micro hardness of the grown crystals was measured using Shimadzu micro hardness tester with a diamond intender. The well-polished crystals were mounted on the platform of the micro hardness tester and loads of different magnitudes (25-100gm) were applied over a fixed interval of time.The Vickers hardness number H_v was calculated from the following expression,

$$H_v = \left(\frac{1.8544*P}{d^2}\right) \quad \text{kg / mm}^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

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.

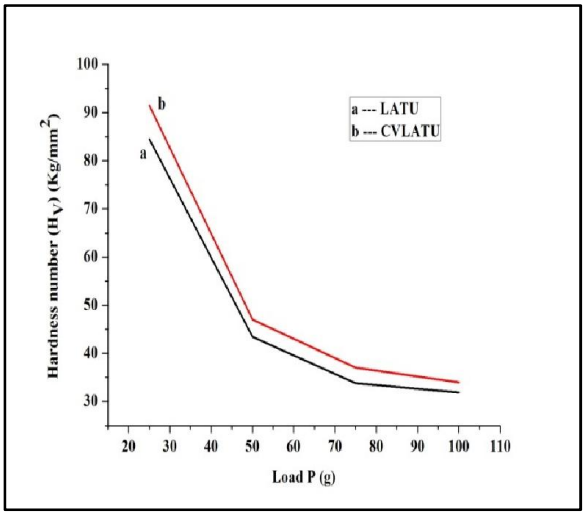

Fig. 15. Variation of hardness with applied loadfor LATU and CVLATU single crystals

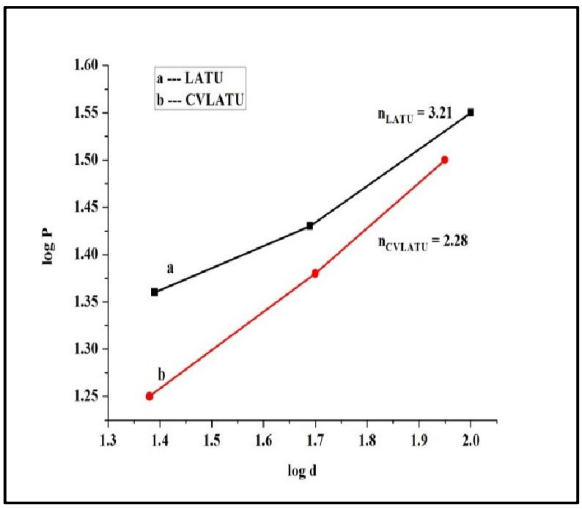

Fig. 16. Variation of log (P) with log (d) for LATU and CVLATU single crystals

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 CVLATU 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 crystal violet 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).

$$P = ad^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

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 CVLATU crystals were found to be 3.21 and 2.28 respectively. According to Onitsch, $1.0 \leq n \leq 0.672$ for hard materials and $n<0.672$ for soft materials (Onitsch, 1956). The observed values of Mayer's index for LATU and CVLATU 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 (Bhagavannarayana and Kushwaha, 2010).

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:

$$\text{Power density (Pd)} = \frac{E}{\tau\pi r^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

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 7.5 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

The SHG conversion efficiency of pure and crystal violet doped LATU crystals was measured by using analog setup as proposed by Kurtz and Perry (Anandan *et al*., 2012) for powder sample. The setup consists of a Q-switched mode locked Nd:YAG laser with fundamental output at 1064 nm, pulserepetition rate 10 Hz, 6 mm beam spot diameter and energy 2.7mJ as input laser of which second harmonics of wavelength 532 nm, generated by a powder sample placed in the path, monitored at the output. After filtering fundamental wavelength, the second harmonic wavelength was fed to the photomultiplier tube and output was measured with digital storage oscilloscope. The second harmonic signals of 384 mV and 576 mV were obtained for pure and crystal violet dye admixtured LATU crystals with reference to KDP (275 mV). Thus, the SHG efficiency of LATU and crystal violet dye admixtured LATU crystals was found to be 1.39 and 2.1 times greater than the standard KDP crystal. The relative SHG efficiency of crystal violet admixtured LATU crystal was found to be 1.5 times higher than that of pure LATU crystal.

Conclusion

Pure and crystal violet dye doped LATU crystals were grown by the slow evaporation method. The presence of crystal violet dopant was confirmed qualitatively by the FTIR spectroscopy. The effect of dopant on the optical properties, crystal structure and SHG efficiency was studied. Dopant modifies the optical transmission, optical band gap, lattice parameters and SHG efficiency of the doped LATU crystal. The SHG efficiency of 0.1 mol% crystal violet dye doped LATU crystal is found to be 1.5 times more as compared to pure LATU. Crystal violet dye doping improves optical transmission, optical band gap and thermal stability. Doped LATU crystal has a higher dielectric constant and lower dielectric loss at higher frequencies. The SHG efficiency and laser damage threshold values were significantly enhanced due to the presence of crystal violet dye in LATU crystal.

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REFERENCES

Anandan, P, Jayavel, R, Saravanan, T, Parthipan, G, Vedhi, C. and Mohan Kumar, R., 2012, 'Crystal growth and characterization of L-histidine hydrochloride monohydrate semiorganic nonlinear optical single crystals', *Optical Materials*, vol. 30, pp. 1225-1230.

Batterman, B.W. and Cole, H, 1964, 'Dynamic diffraction of X-rays by perfect crystals', *Rev. Mod. Phys*., vol. 36, pp. 681-717.

Bella, S.D., 2001, 'Second-order nonlinear optical properties of transition metal complexes', *Chem. Soc. Rev.,* 30, 355.

Bhagavannarayana, G and Kushwaha, S.K., 2010, 'Enhancement of SHG efficiency by urea doping in ZTS single crystals and its correlation with crystalline perfection as revealed by Kurtz powder and high-resolution X-ray diffraction methods', *J. Appl. Crystallogr.,* vol. 43, pp. 154-162.

Bhagavannarayana, G, Kushwaha, S.K, Shakir, M. and Maurya, K.K., 2010, "Effect of necking on Czochralski-grown LiF crystals and its influence on crystalline perfection and the correlated physical properties", *J. Appl. Crystallogr.*, vol. 44, pp. 122-128.

Bhagavannarayana, G., Parthiban, S. and Meenakshisundaram, S., 2008, "An interesting correlation between crystalline perfection and second harmonic efficiency on KCl – and Oxalic acid doped- doped ADP crystals", Cryst. Growth Des., 8, 446.

Blau, W., 1987, 'Organic materials for nonlinear optical devices', *Phys. Technol.,* 18, 250.

Cole, J.M., Wilson, C.C., Howard, J. A. and Cruickshank, F.R., 'Rapid neutron-diffraction data collection for hydrogen-bonding studies: application of the Laue diffractometer (LADI) to the case study zinc (tris)thioureasulfate', *Acta Crystallogr.* B56 (2000) 1085.

Dhumane, N.R., Hussaini, S.S., Kunaldatta, Prasantaghosh and Mahendra, Shirsat, D., 2010, "Growth and characterization of nonlinear optical Crystal Bis thiourea cadmium chloride (BTCC) in presence of L-Alanine", J. *Pure Appl. & Ind. Phy*s., vol. 1, pp. 45-52.

Fan, Y. X., Eckardt, R. C., Byer, R. L., Rout, R. K. and Feigelson, R.S., 1984, 'Nonlinear Infrared Frequency Conversion in AgGaS2 and AgGaSe2', *Appl. Phys., Lett*. 45, 313.

He, G.S. and Liu, H., 'Physics of Non-Linear Optics', 1999, World-Scientific, Singapore.

Hussaini, S.S., Dhumane, N.R., Dongre, V. G. and Shirsat, M.D., 2009, 'Growth and characterization of glycine doped bis thiourea cadmium chloride single crystal', *J. Mater.Sci., Poland,* 27, 365.

Kar, S., Bhatt, R., Bartwal, K.S. and Wadhawan, V.K., 2004, 'Investigations on crystalline and optical perfection of SHG oriented KDP crystals', *Cryst. Res. Technol.,* 39, 230.

Lal, K. and Bhagavannarayana, G., 1989, 'A high-resolution diffuse X-ray scattering study of defects in dislocation free silicon crystals grown by the float-zone method and comparison with Czochralski-grown crystals', *J. Appl. Cryst.,* vol. 22, pp. 209-215.

Marder, S.R., Sohn, J.E. and Stucky, G.D., 1991, 'Material for Nonlinear Optics', *American Chemical Society,* Washington, DC.

Onitsch, E.M., 1956, "The present status of testing the hardness of materials", *Mikroskopie.,* vol. 95, pp. 12-14.

Palanisamy, S and Balasundaram, O.N., 2008, 'Growth, Optical and Mechanical Properties of Alanine Sodium Nitrate (ASN)', *Rasayan Journal of Chemistry*, vol. 1, pp. 782-787.

Prasad, P.N. and Williams, D.J., 1991, 'Introduction to Nonlinear Optical Effects in Molecules and Polymers', John-Wiley Sons Inc., New York.

Pritula, I.M., Gayvoronsky, V., Gromov, Yu., Kopylovsky, M., Kolybaeva, K.,Puzikov, V., Kosinova, A., Savvin, Yu., Velikhov, Yu. andLevchenko, A., 2009, "Linear and nonlinear optical properties of dyedoped KDP crystals: Effect of thermal treatment", *Opt. Commun.,* 282, 1141.

Pritula, I.M., Velikhov, Yu., Levchenko, A.N., Kolybayeva, M., Puzikov, V.M., Tyutyunnik, V.B. and Doroshenko, A.M., 2004, *Funct. Mater*., 1(4), 701.

Rajesh, P., Ramasamy, P., Kumar, K. and Bhagavannarayana, G., 2010, "Effect of cobalt and DL-Malic acid on the growth rate, crystalline perfection, optical, mechanical, dielectric, piezoelectric properties and SHG efficiency of ADP single crystals", *Physica B*, 405, 2401.

Raju, B., Saritha, A., Bhagavannarayana, G. and Hussain, K.A., 2011, "A comparative study on growth, structural, optical, thermal and mechanical properties of undoped and dye doped bis glycine cadmium chloride single crystals", *J. Cryst.Growth.,* 324, 184.

Ramajothi, J. and Dhanuskodi. S., 2007, 'Crystal growth, thermal and optical studies on a semiorganic nonlinear optical material for blue-green laser generation', Spectrochimica Acta part A, vol. 68, pp. 1213-1219.

SwetaMoitra and TanusreeKar, 2007, 'Growth and characterization of pure and potassium chloride-doped Zinc Tris–thiourea Sulphate (ZTS) single crystals', *Opt. Mater*., 30, 508.

Vries de, S.A., Goedtkindt, P., Bennett, S.L., Huisman, W.J., Zwanenburg, M.J., Smilgies, D.M., De Yoreo, J.J., Enckevort van, W.J.P., Bennema, P. and Vlieg, E., 1998, 'Surface Atomic Structure of KDP Crystals in Aqueous Solution: An Explanation of the Growth Shape', *Phys. Rev. Lett.,* 80, 2229.

Wang, X.Q., Xu, D., Yuan, D.R., Tian, Y.P., Yu, W.T., Sun, S.Y., Yang, Z.H., Fang, Q., Lu, M.K., Yan, Y.X., Meng, F.Q., Guo, S.Y. and Guo., Zhang, G.H. and Jiang, M.G., 2003, Synthesis, structure and properties of a new nonlinear optical material: zinc cadmium tetrathiocyanate', Mater. Res. Bull., 34.

Winkler, E., Etchegoin, P., Fainstein, A. and Fainstein, C., 2000, 'Resonant Raman scattering and optical transmission studies of Cu(II) and Fe(III) impurities in crystalline L-alanine', *Phys. Rev.,* B, 61, 15756.

Zaitseva, N. and Carman, L., 2001, "Rapid growth of KDP-type crystals", Prog. Cryst. Growth Charact', 43,1.

Zernike, F. and Midwinter, J.E., 1973, 'Applied nonlinear optics', John-Wiley Sons Inc., New York, New York.

Zyss, J. and Chemla, D.S., 1987, 'Nonlinear Optical Propertiesof Organic Molecules and Crystals', Academic Press, New York.

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