

Studies on Growth, Structural, Luminescence, Linear and Nonlinear Optical Properties of Bisthiourea Lithium Zinc Sulphate Single Crystal for Optoelectronics Applications

R. PUNNIAMOORTHY^{1,*}, A. FRANKLIN ALEX JOSEPH², A. SATISH³,
M. CHITRAVEL³, A. VENGADESAN⁴, G. PASUPATHI⁵ and S.S. SYED ABUTHAHIR⁶

¹Department of Physics, St. Joseph's College of Engineering and Technology (Affiliated to Anna University, Chennai), Elupatti, Thanjavur-613403, India

²Department of Electrical and Electronics Engineering, St. Joseph's College of Engineering and Technology (Affiliated to Anna University, Chennai), Elupatti, Thanjavur-613403, India

³Department of Chemistry, St. Joseph's College of Engineering and Technology (Affiliated to Anna University, Chennai), Elupatti, Thanjavur-613403, India

⁴Department of Electrical and Electronics Engineering, Sri Venkateshwaraa College of Engineering and Technology (Affiliated to Pondicherry University), Ariyur, Pondicherry-605102, India

⁵PG and Research Department of Physics, A.V.V.M. Sri Pushpam College (Autonomous) (Affiliated to Bharathidasan University, Tiruchirappalli), Poondi, Thanjavur-613503, India

⁶Department of Chemistry, Jamal Mohamed College (Autonomous) (Affiliated to Bharathidasan University, Tiruchirappalli), Tiruchirappalli-620020, India

*Corresponding author: E-mail: dr.rpmoorthy359@gmail.com

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Bisthiourea lithium zinc sulfate (BTLZS) single crystals have remarkable nonlinear optical properties. The crystals were prepared using slow evaporation of solution growth techniques (SEST). The crystal structure and crystalline properties of the synthesized crystals was conducted with powder XRD and SCXRD techniques, respectively. The orthorhombic system of BTLZS crystal has been identified with space group $Pca2_1$. The existence of vibrational functional groups in the synthesized crystal was confirmed by FTIR spectroscopy. The optical parameters were determined through UV-Vis-NIR transmission spectra. The synthesized BTLZS demonstrated that the emission of green light at 581 nm within its photoluminescence (PL) spectra. The Kurtz and Perry powder method serves as a means to explore the nonlinear optical properties of synthetic crystals. The enhanced second harmonic generation (SHG) has 1.63 times more efficiency than standard postassium dihydrogen phosphate (KDP) crystal. The analysis on thermal and laser damage thresholds shows that this crystal demonstrates stability and holds promise for applications in optoelectronic devices.

Keywords: Crystal growth, Orthorhombic phase, NLO crystal, Laser damage threshold, Thermal properties.

INTRODUCTION

Photonic and optoelectronic equipment and devices using nonlinear optical (NLO) supply have gained interest in recent years. This demand has increased research on making these supplies [1-3]. Many workers have been searching for new materials, both organic and inorganic, to meet the rising need for effective NLO materials for these kinds of applications. Concerns about these two types of materials have just recently spread to the study of semiorganic NLO materials, which have

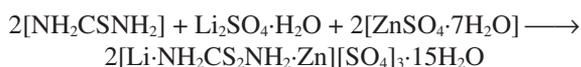
great thermal and mechanical characteristics, a high second harmonic conversion efficiency and a significant polarizability [4,5]. High purity zinc vitriol ($ZnSO_4 \cdot 7H_2O$) and other heptahydrate sulfate materials have recently emerged as a promising topic of study with potential commercial and scholarly uses in fields as diverse as agriculture, medicine and chemistry [6]. The typical formula for zinc vitriol is $RSO_4 \cdot 7H_2O$, where R is an elemental formula for zinc, nickel, magnesium or both. Among the class of inorganic nonlinear optical crystals, $ZnSO_4 \cdot 7H_2O$ is included [7,8]. Furthermore, zinc vitriol is utilized in

various applications, including fertilizers, electrolytes for zinc plating, lithopone production, skin and leather preservation, dye mordants, and medicinal purposes such as astringents and emetics. It is significant to observe that thiourea can produce hydrogen bonds and has a significant dipole moment, therefore it is possible that crystals with non-centrosymmetric space groups will form when it combines with metal halides. Crystals containing thiourea have a wide range of inherent flaws, although they are great for boosting second harmonic generation (SHG) efficiency [9-11]. A stable compound with high optical non-linearity and accurate physicochemical method may be formed by easily integrating metals like zinc, cadmium and mercury with thiourea [12,13]. Several metal-thiourea complexes have shown promise for NLO properties, including BTZF, TTZCS, TTMZS, TPMS, BTLKS and BTSZS [14-19].

Many workers generally used slow evaporation to synthesize bithiourea lithium zinc sulfate single crystals at ambient temperature. The utilization of lithium ions in a multitude of semiorganic crystals can be attributed to their superior charge density relative to other alkali metals as well as their compatibility with both organic and inorganic complexes. Several lithium sulfate combined materials have been proposed to improve SHG efficacy. Such materials consist of lithium sulfate monohydrate, glycine lithium sulfate and lithium sulfate monohydrate that has been doped with EDTA [20-23]. Among these materials, bithiourea lithium zinc sulfate stands out as a crystal that has fascinating potential in the field of optoelectronics. In terms of transparency, thermal stability and NLO efficiency, it is superior than various thiourea-based metal complex crystals that have been reported earlier [24]. Based on the literature, this is the first synthesis of bithiourea lithium zinc sulfate (BTLZS) having unique semiorganic single crystals. Following that, several characterization like Fourier transform infrared spectroscopy (FTIR), single crystal X-ray diffraction (SCXRD), ultraviolet visible-near infrared (UV-Vis-NIR), photoluminescence (PL), second harmonic generation (SHG), laser damage threshold (LDT) and thermal (TG/DTA) analysis were carried out.

EXPERIMENTAL

Synthesis and solubility of BTLZS: In order to synthesize bithiourea lithium zinc sulfate (BTLZS) salt, 2:1:2 stoichiometric ratio was utilized in double-distilled water. In brief, analytical grade thiourea ($\text{CH}_4\text{N}_2\text{S}$), lithium sulfate monohydrate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) and zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) solutions were mixed thoroughly at room temperature [19]. The produced chemical undergoes the following reaction:



The solubility experiment utilized finely powdered BTLZS. To successfully generate bulk single crystals using the solution growth process, the material must be soluble in a certain solvent. Solubility tests were conducted at varying temperatures utilizing a combination of double distilled water and an alternative solvent. A solution of recrystallized BTLZS salt was slowly added to 100 mL of water at 30 °C with constant stirring. Upon

reaching saturation, the gravimetric procedures were conducted to evaluate the equilibrium concentration of the solute. The solubility was determined at different 35, 40, 45 and 50 °C (Fig. 1).

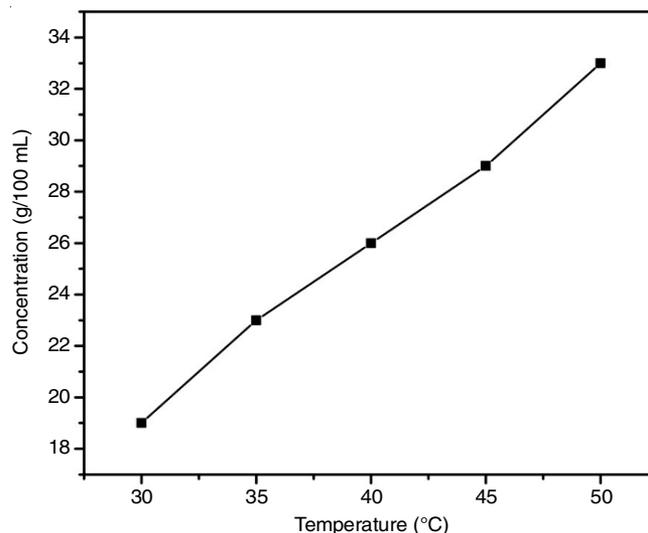


Fig. 1. Curve of solubility for BTLZS compound

Crystal growth: The findings of the solubility test indicate that BTLZS salt is one of the substances that dissolves more readily in water. After dissolving the minimum quantity of all compounds, a homogeneous mixture was achieved by utilizing Millipore water and a magnetic stirring device for 3 h. More than four recrystallizations were performed on the synthesized NLO material to achieve the maximum purity. After recrystallization, the solution was filtered and evaporated at 303 K. Fig. 2 illustrates that after a period of 20 to 25 days, the parent solution produced the most superior BTLZS transparent single crystals, measuring 6 mm × 6 mm × 3 mm.



Fig. 2. Single crystals of BTLZS

RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis (SCXRD): The ENRAF NONIUS CAD4 X-ray diffractometer was employed to evaluate the structural properties of the prepared BTLZS crystal by employing $\text{MoK}\alpha$ (0.71073 Å) radiation. The results indicated that the crystal is orthorhombic and has the $Pca2_1$ space group. Based on the data shown in Table-1, the parameters of the unit cell display a significant degree of agreement with the values that were previously determined [19].

TABLE-1
LATTICE PARAMETERS OF BTSZS AND BTLZS

Samples	a (Å)	b (Å)	c (Å)	Volume (Å ³)	Crystal system	Space group
BTSZS [Ref. 19]	7.78	11.13	15.51	1343	Orthorhombic	–
BTLZS	7.84	11.21	15.60	1371	Orthorhombic	Pca2 ₁

Powder XRD: An XPERT-PRO diffractometer (40 kV and 30 mA; CuK α radiation with a wavelength of 1.54060 Å) was used to evaluate the crystallinity and purity of phases. The sample was scanned at 1°/min from 10° to 80°. The index pattern of powder XRD in the BTLZS is shown in Fig. 3, which consist of strong peaks indicating the strong crystallinity of the prepared BTLZS material.

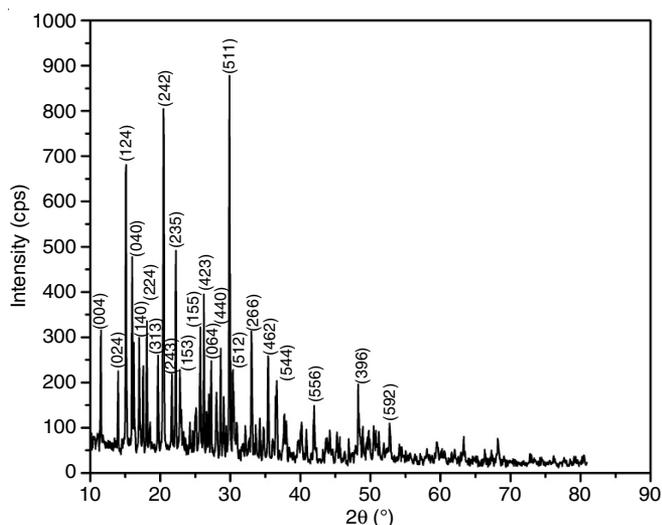


Fig. 3. Powder XRD index pattern of BTLZS single crystal

Vibrational studies: A Perkin Elmer analyzer using KBr pellet method was used to obtain the FTIR spectrum of the BTLZS single crystal in the wavelength range of 4000 and 400 cm⁻¹. The spectrum (Fig. 4) shows that NH₂ groups have symmetric and asymmetric stretching modes at 3380 and 3196 cm⁻¹ [18]. The intrinsic characteristic peak of thiourea having NH was detected in 2716-1815 cm⁻¹ range, where as a vibration band for NH₂ bending is observed at 1628 cm⁻¹. The bidentate ligand properties of thiourea cause a shift to lower frequencies of 716 cm⁻¹ and 1401 cm⁻¹ in its C=S symmetric and asymmetric stretching vibrations. The interaction between metal ions and the NH₂ group is significantly improved due to the delocalization of π -electrons, which lead to an increase in the stretching frequencies of symmetric and asymmetric N-C-N structures. The peak at 1512 cm⁻¹ corresponds to the N-C-N symmetric stretching vibration of thiourea is also shifted from originally at 1470 cm⁻¹. It is clear that NH₂ has a rocking vibration because of the large peak at 1031 cm⁻¹. The symmetric and asymmetric frequencies identified at 954 and 1123 cm⁻¹ served as the foundation for the identification of the significant SO₄ group which was already present in the synthesized crystals. The N-C-S also exhibits the bending vibrations at 473 cm⁻¹ and 618 cm⁻¹, respectively. The symmetric bending and asymmetric stretching vibrations linked with SO₄²⁻ are shown by the peaks at 473 cm⁻¹ and 618 cm⁻¹, respectively [25,26]. Thus,

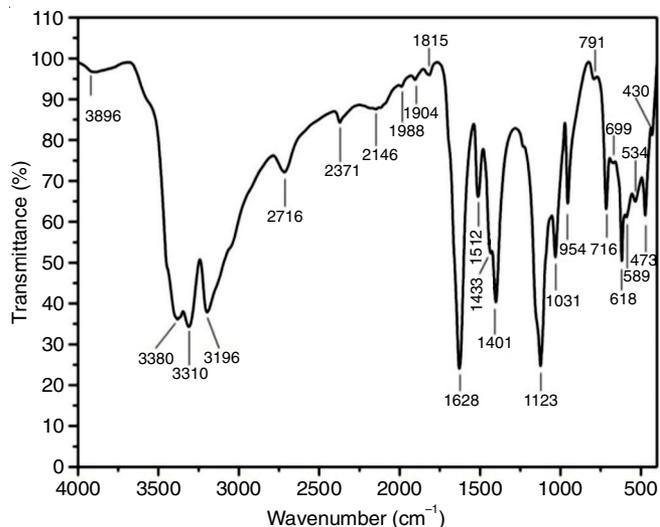


Fig. 4. FTIR BTLZS crystal spectrum

it is confirmed that the metal interacts with thiourea through the sulfur atom. The other functional groups present in the materials are specified in Table-2.

TABLE-2
VIBRATIONAL ASSIGNMENTS OF BTLZS

Thiourea [Ref. 27]	Li ₂ SO ₄ ·H ₂ O [Ref. 28]	BTLZS	Frequency assignments
3376	–	3380	$\nu_{as}(\text{NH}_2)$
3167	–	3196	$\nu_s(\text{NH}_2)$
–	–	2716	$\nu(\text{N-H})$
–	2140	2146	$\nu(\text{OH})$
–	–	1815	$\nu(\text{N-H})$
1628	1638	1628	$\delta(\text{NH}_2)$
1470	–	1512	$\nu_s(\text{N-C-N})$
1414	–	1401	$\nu_{as}(\text{C=S})$
1089	1125	1123, 1031	$\rho(\text{NH}_2)/\gamma_{as}(\text{SO}_4)$
–	–	954	$\nu_s(\text{SO}_4)$
740	–	791, 716	$\nu_s(\text{C=S})$
–	615	618	$\delta_{as}(\text{N-C-S})/\gamma_{as}(\text{SO}_4)$
469	479	473	$\delta_s(\text{N-C-S})/\gamma_{sb}(\text{SO}_4)$

ν_s = symmetric stretching, ν_{as} = asymmetric stretching, δ = bending, δ_s = symmetric bending, δ_{as} = asymmetric bending, ρ = rocking.

Linear and nonlinear optical studies

UV-Vis-NIR spectral studies: For maximum visualization, the nonlinear optical (NLO) crystals need a broad transparency range without absorption and a low cut-off wavelength of 190-400 nm [29]. The Perkin-Elmer Lambda 35 spectrometer was used to acquire BTLZS crystal optical transmission spectrum in the range of 190 to 1100 nm. Fig. 5 shows that the synthesized crystal has a 400-1100 nm optical spectrum and a 290 nm cutoff wavelength. This characteristic is highly desire for the optoelectronic device fabrication.

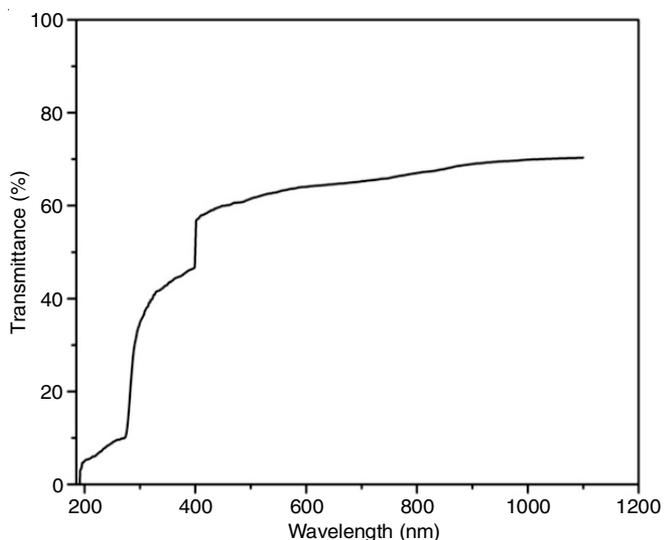


Fig. 5. Transmittance spectrum of grown crystal

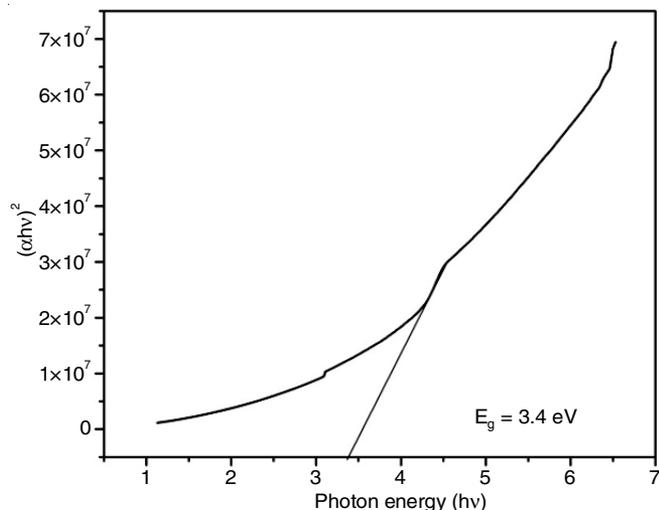
The examination of the optical absorption coefficient in relation to photon energy provides insights into the material's band structure and the dynamics of electron transitions. Using the subsequent equation to calculate the absorption coefficient (α) based on the observed transmittance (T):

$$\alpha = \frac{2.306 \log(1/T)}{t} \quad (1)$$

In contrast to the thickness of crystal, measured at 3 mm; T denotes the amount of light that can flow through it. The crystal displays a direct band gap, characterized by an optical absorption coefficient (α) consistent with the following equation [30]:

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \quad (2)$$

where h stands for Planck's constant; ν denotes the frequency of incident photons; E_g refers to the optical band gap; and A represents an arbitrary constant. A plot of $(\alpha h\nu)^2$ vs. $h\nu$, as shown in Fig. 6, indicates that the optical band gap (E_g) of the BTLZS crystal is 3.4 electron volts. The extinction coefficient (K) was calculated using eqn. 3:

Fig. 6. Photo energy (hv) vs. $(\alpha h\nu)^2$

$$K = \frac{\alpha \lambda}{4\pi} \quad (3)$$

Fig. 7 demonstrates that as photon energy increases, there is a corresponding rise in the extinction coefficient. Thus, based on the results, the synthesized crystal is an ideal contender for use in nonlinear optics and optoelectronic systems.

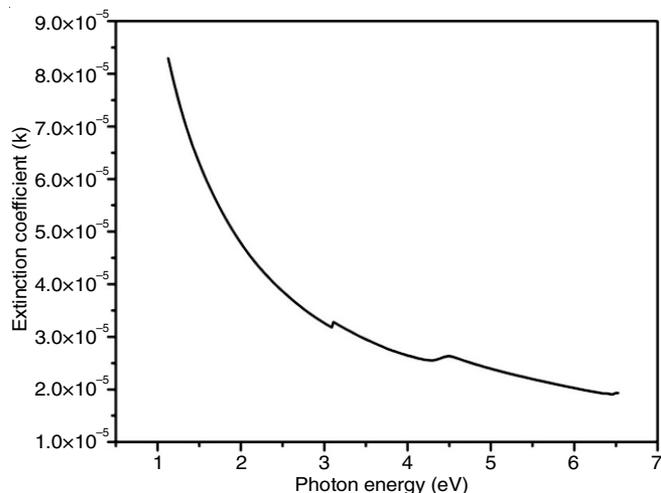


Fig. 7. Photon energy (eV) vs. extinction coefficient (k)

Photoluminescence studies: The photoluminescence (PL) spectrum were taken at room temperature using a Perkin-Elmer LS-45 photoluminescence spectrometer at 290 nm. Fig. 8 shows that the spectrum were recorded between 300 and 700 nm. Due to its noncentrosymmetric properties, the BTLZS crystal shows the green fluorescence in its emission spectra, which is associated with a distinctive colour emission peak at 581 nm. The reason is attributed to the π - π^* transition caused by metal ion-ligand molecule interaction [31]. The green emission in the PL spectrum analysis showed that the BTLZS crystal had nonlinear optical (NLO) capabilities. Kurtz and Perry's second harmonic generation (SHG) measurement also confirmed the result. Thus, the prepared crystal is appropriate for the luminous and optoelectronic applications [32-34].

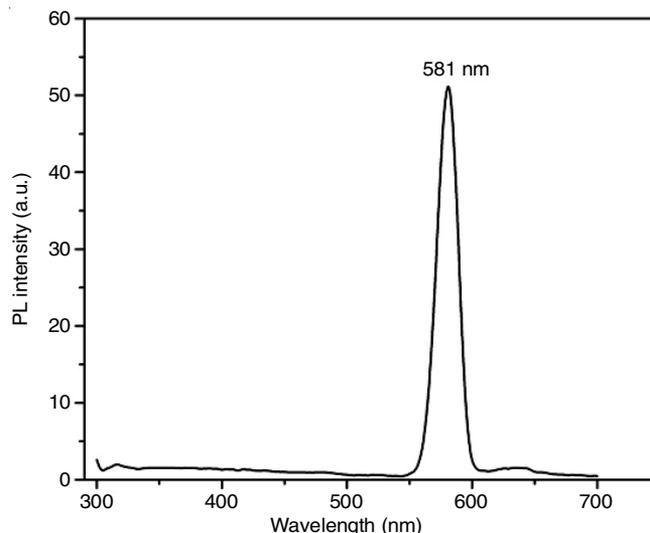


Fig. 8. Luminescence spectrum of BTLZS crystal

Investigations into nonlinear optical phenomena: The Kurtz and Perry powder technique determines the nonlinear optical characteristics of the prepared BTLZS. The powdered sample was irradiated with a Q-Switched Nd:YAG laser at 1064 nm, 6 ns pulse width and 10 Hz repetition rate. The sample is put in a cell holder and sandwiched between the two clear glass plates. A photomultiplier tube generated the green-emitting harmonic generation signal (second) at 532 nm within the sample [35,36]. The reference material consists of uniformly sized KDP crystals. The powdered sample was subjected to a laser energy of 0.70 J. In contrast to 8.94 mJ produced by KDP material, the output energy of the prepared BTLZS material was 14.6 mJ. Thus, The efficiency of second harmonic generation of BTLZS crystal is 1.63 times that of KDP material. The BTLZS exhibits superior SHG efficiency relative to certain thiourea metal complex crystals, due to the interaction between thiourea and lithium and zinc ions, which have inherent NLO characteristics, as shown in Table-3. This study confirmed the nonlinear optical characteristics of the specified compound.

TABLE-3
COMPARATIVE SHG EFFICIENCY OF
TPMS, TTMZS, BTSZS AND BTLZS

Samples	SHG efficiency with respect to KDP	Ref.
TPMS	0.91	[17]
TTMZS	1.20	[16]
BTSZS	1.30	[19]
BTLZS	1.63	Present study

Threshold for laser-induced damage studies: The effectiveness of harmonic conversion depends on the energy of the incoming beam. Therefore, it is essential determine the incoming beam at the crystal with accuracy. The convergence process can lead to severe impact to the material, known as the damage threshold. The laser damage threshold (LDT) is an essential parameter that requires thorough testing during the production of optical devices. The LDT is influenced by several factors such as optical absorption, thermal conductivity, specific heat, *etc.* A material characterized by a significant specific heat capacity will demonstrate an elevated latent heat of transformation. The material exhibiting significant LDT is in high demand for the manufacturing of optical devices, owing to its exceptional linear and nonlinear optical properties [37]. A 3 mm BTLZS crystal was put on a sample holder and irradiated by a 1064 nm Q-switched Nd:YAG laser. A 30 sec exposure with a 6 ns pulse width was used. The repeating rate is 10 Hz. With the help of EPM 2000 instrument, the energy output and power were measured. The following formula was applied to calculate the LDT:

$$P = \frac{E}{\tau \pi r^2} \quad (4)$$

where P is the power density of 8.924 GW/cm²; E is the energy in joules; τ is the pulse width in nanoseconds; and r is the laser beam spot radius in micrometers. Table-4 compares the LDT value of the synthesized crystal with other relevant materials and when compared to standard KDP and other thiourea metal

TABLE-4
THE LDT VALUES OF CERTAIN WELL KNOWN CRYSTALS

Crystal	Laser damage threshold (GW/cm ²)	Ref.
KDP	0.200	–
Urea	1.500	[38]
BTCC	6.000	[39]
BTCF	7.623	[40]
BTLZS	8.924	Present study

complex crystals, BTLZS has a superior LDT. Consequently, the synthesized crystal is ideally suited for applications that require high power frequency conversion.

Thermal studies: The thermal (TGA and DTA) studies were performed on the BTLZS crystal using NETZSCH STA 409F3 equipment. The experiment was conducted in a nitrogen atmosphere in the temperature range of 30 to 1100 °C at the heating rate of 30 K/min. The TGA curve delineates five distinct steps involved in the process of weight loss. At 96.4 °C, an initial weight reduction of approximately 4% occurs as a result of the evaporation of physically absorbed lattice water. Within the temperature spectrum of 96.4 °C to 226.4 °C, one observes an absence of weight loss. In the second stage, which lasted from 226 °C to 331.4 °C, there was a significant 57% decrease in weight. A sharp drop in mass observed between 331.4 °C and 1011.4 °C, is due, in part, to the emission of NH₂, sulfur oxide, nitrogen, carbon, sulfate and CO₂, among other volatile compounds (Fig. 9).

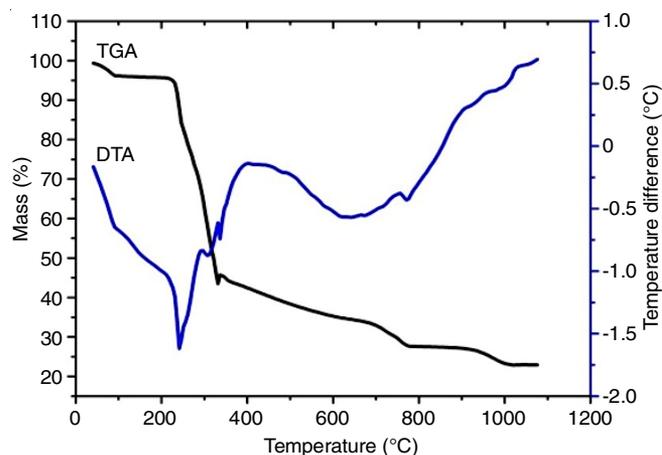


Fig. 9. TG/DTA curve of BTLZS crystal

At 241.4 °C, the melting point of the material, the DTA curve reveals an endothermic peak. Furthermore, reversible endothermic peaks at 311.4, 336.4 and 771.4 °C were also detected, suggesting that the formed crystal has decomposed significantly. There is a strong correlation between the DTA curve and the substantial mass loss observed by the TG curve [41,42]. However, a thiourea-metal combination in the interior coordination sphere indicates an improved crystal stability.

Conclusion

A novel bisthiourea lithium zinc sulfate (BTLZS) single crystal was synthesized using slow solvent evaporation method at room temperature. The single crystal X-ray diffraction analysis (SCXRD) shows that the material is orthorhombic

and contains Pca_2 , a non-centrosymmetric space group. Whereas the XRD analysis showed that BTLZS is pure and crystalline. The prepared BTLZS crystals have high optical transmittance and a cut-off wavelength of 290 nm, making them ideal for nonlinear optical applications. By measuring the extinction coefficient (k), the optical band gap was found to be 3.4 eV. Photoluminescence spectra demonstrate the BTLZS produce green light. The Kurtz and Perry approach showed that BTLZS has 1.63 times the powder SHG efficiency of KDP. It has been found that the energy density is 8.924 GW/cm² indicating a tremendous degree of intensity. The thermal studies showed that the prepared crystals had thermal stability up to 241 °C.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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