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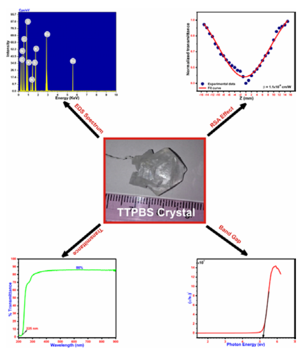
ABSTRACT

A novel tris (thiourea) potassium barium sulphate (TTPBS) complex has been synthesized and the complex formation was confirmed by means of spectroscopic analysis. The TTPBS single crystal has been grown by most commercial slow solvent evaporation method. The single crystal X-ray diffraction technique has been employed to confirm the crystal structure and unit cell dimensions of TTPBS crystal. The functional groups of grown crystal have been identified by means of Fourier transform infrared analysis. The constituent elements of title crystal have been determined by means of EDS technique. In UV–visible studies the TTPBS crystal has been testified within 200–900 nm to examine the optical transparency and determine the optical band gap. The frequency conversion efficiency of TTPBS crystal has been assessed by means of Kurtz-Perry test. He–Ne laser assisted Z-scan technique has been employed to ascertain the third order nonlinear optical (TONLO) refraction and absorption effect in TTPBS crystal. The magnitude of TONLO refractive index (n_2), absorption coefficient (β) and susceptibility (χ^3) of title crystal has been illustrated using the Z-scan data. The Nd:YAG laser facilitated surface damage threshold of TTPBS crystal has been determined and it is found to be in MW/cm^2 range.



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Crystal growth; optical studies; nonlinear optical materials; organometallic crystal

1. Introduction

Crystal engineering is mature but still the most tempting and rapidly advancing filed of research [1]. The current and futuristic technological era demands uncompromised efforts for designing, tuning and modeling novel hybrid nonlinear optical (NLO) materials which can withstand high mechanical loads, extensive thermal environment and high power laser exposure at the same time it must offer large NLO coefficient, fast electronic response time, extended design flexibility and structural diversity. The aforesaid features mutually occur in abundance in semiorganic single crystals and thus become crucial asset for applications in quantum electronics, optical communications, computations, data storage, image processing, optoelectronics and photonic devices [2–6]. Amongst the available wide spread class of semiorganic NLO crystals thiourea metal complex (TMC) crystals certainly gain more attention owing to large symmetrical diversity, excellent optical properties and impressive physico-chemical features. Thiourea is realized to be one of the ideal building block compounds which possesses an ability of large dipole moment in addition it can easily coordination with metal through ligand of sulphur and oxygen to construct new acentric metal-organic compounds [7–9]. The scientific fraternity involved in field of crystal designing and engineering have proposed various ideas which include unique design

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methodologies, different growth techniques and adapted distinctive research approach to unearth the best qualities of TMC crystals which play crucial role to realize their exclusive utility for potential device applications [10–14]. Large series of TMC crystals include calcium bis-thiourea chloride (CBTC) [15], potassium thiourea iodide (PTI) [16], bis-thiourea zinc bromide (BTZB) [17], bis-thiourea cadmium iodide [18], bis-thiourea zinc acetate (BTZA) [19], bis-thiourea cadmium chloride (BTCC) [20], bis-thiourea barium chloride (BTBC) [21], dichloro tetrakis thiourea nickel chloride [22], tris-thiourea zinc sulphate (ZTS) [23], tris-thiourea magnesium sulphate (MTS) [24] and bis-thiourea nickel barium chloride [25]. The TMC crystals demonstrate huge technological impetus therefore our group firstly attempts to synthesize and grow a novel semiorganic NLO crystal, tris-thiourea potassium barium sulphate (TTPBS). The investigation on TTPBS crystal have been accomplished by employing single crystal XRD, Fourier transform infrared (FTIR), energy dispersive spectroscopy (EDS), UV–visible, Kurtz-Perry test, Z-scan and laser damage threshold characterization techniques.

2. Synthesis and crystal growth

To synthesize the TTPBS complex the Merck make AR grade thiourea, potassium sulphate and barium sulphate materials were slowly dissolved in double distilled water in the molar ratio 3:1:1. Further, to avoid the co-precipitation and facilitate homogeneous reaction of all the constituents the mixture solution was allowed to stir well for eight hours. This mixed solution was then carefully filtered in the clean rinsed beaker using the No. 1 Whatman filter paper and the filtrate was covered with the perforated coil. The beaker containing the filtrate was then placed in the constant temperature bath maintained at 32 °C to facilitate slow solvent evaporation. The good quality TTPBS seed crystals were harvested within the period of 13 days. TTPBS single crystal of size $20 \times 15 \times 10$ mm^3 shown in Figure 1 was grown within three weeks by hanging the seed crystal in saturated solution of TTPBS.

3. Results and discussion

The structural analysis of TTPBS crystal has been carried out at room temperature using the Enraf Nonius CAD4 single crystal X-ray diffractometer. The experimentally determined crystallographic data of thiourea and TTPBS crystal is shown in Table 1. It reveals that the title crystal crystallizes with orthorhombic structure however noticeable fact is that the TTPBS crystal is found to have marginally larger volume as compared to thiourea crystal. The large change in lattice parameters might have been observed due to coordination of thiourea with potassium and barium metal ions through bonds of sulphur and oxygen.

Figure 1. Single crystal of TTPBS.

The FTIR spectral analysis has been performed using the JASCO FTIR-4000 series spectrophotometer to determine the modes of vibration of functional groups associated with title crystal. The FTIR spectrum recorded in the range of 500–4000 cm^{-1} is shown in Figure 2(a). The N–C–S bond bending vibration associated with thiourea is contributed at wavenumber 510 cm^{-1}. The absorption peak contributed at 615 cm^{-1} is assigned to C–C bond deformation. The mild absorption peak evident at 673 cm^{-1} is assigned to C–C–CHO bending vibration. The C = S stretching vibration is evident at 720 cm^{-1}. The prominent absorption peak observed at 1079 cm^{-1} is contributed by S = O bond stretching vibration. The stretching of N = N bond is observed at 1404 cm^{-1}. The stretching of N–C–N bond is attributed at 1463 cm^{-1}. The symmetric and asymmetric stretching modes of NH_2 bond are evident at 1601 and 2683 cm^{-1}. The N–H bond stretching mode of vibration is observed at 3168, 3271, 3374 and 3729 cm^{-1}.

The element detection of TTPBS crystal material has been performed by means of EDS technique using the Hitachi S4700 instrument. Initially the selected TTPBS single crystals were powdered and the powder sample was subjected to EDS analysis. The EDS spectrum has been recorded in the range of 0–10 keV and the identified elements at the respective energy peaks are depicted in Figure 2(b). In addition to H-bonding network the coordination of metal ions is manifested by sulphur and oxygen bonds of thiourea. The observed energy peaks of carbon, nitrogen, sulphur, oxygen, barium and potassium confirms the presence of all the elements of newly formed TTPBS meal-organic complex crystal.

The optical transparency is the most decisive and inherent quality which is chiefly credited in the material owing to photoactive molecular chromophores and the allowed transition of electrons to discrete energy states (from ground state to σ and π states) [26–29]. However, in bulk crystal the physical parameters that play decisive role in determining the limit of optical transmittance are (a) molecular alignment along the crystal plane [30,31] and (b) structural and crystalline defects (voids, vacancies, solvent inclusions, striations, grain boundaries) [32–34]. Ideally fabrication of NLO devices demand highly transparent material and in order to examine the transparency of TTPBS crystal the UV–visible spectral analysis has been undertaken using the Shimadzu UV–2450 spectrophotometer. The TTPBS crystal (1.5 mm thickness) has been scanned in the range of 200–900 nm and the recorded transmittance spectrum is shown in Figure 3(a). It reveals that the highest transmittance offered by grown crystal is up to 86% and the transmittance cut-off is attributed at 225 nm. The optical scattering/absorption in crystal medium due to defect reduces the optical transmittance of the crystal [35], however the observed uniform and high optical transmittance throughout the spectral range indicates that the grown crystal possess good optical homogeneity and lesser defect centers. The dependency of linear absorption coefficient (α) on incident photon energy ($h\nu$) is obvious from equation, $(\alpha h\nu)^2 = A\,(h\nu - E_g)$ which helps to realize the presence of optical band gap (E_g) in the material. Taucs plot shown in Figure 3(b) reveals that the E_g of TTPBS crystal is 5.16 eV. The lower cut-off wavelength, wide optical band gap and high optical transmittance of TTPBS crystal exactly meets

Table 1. Single crystal XRD data.

Crystal	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å)^3	Structure
Thiourea	7.65	8.54	5.47	357.36	Orthorhombic
TTPBS	5.79	7.49	10.09	438	Orthorhombic

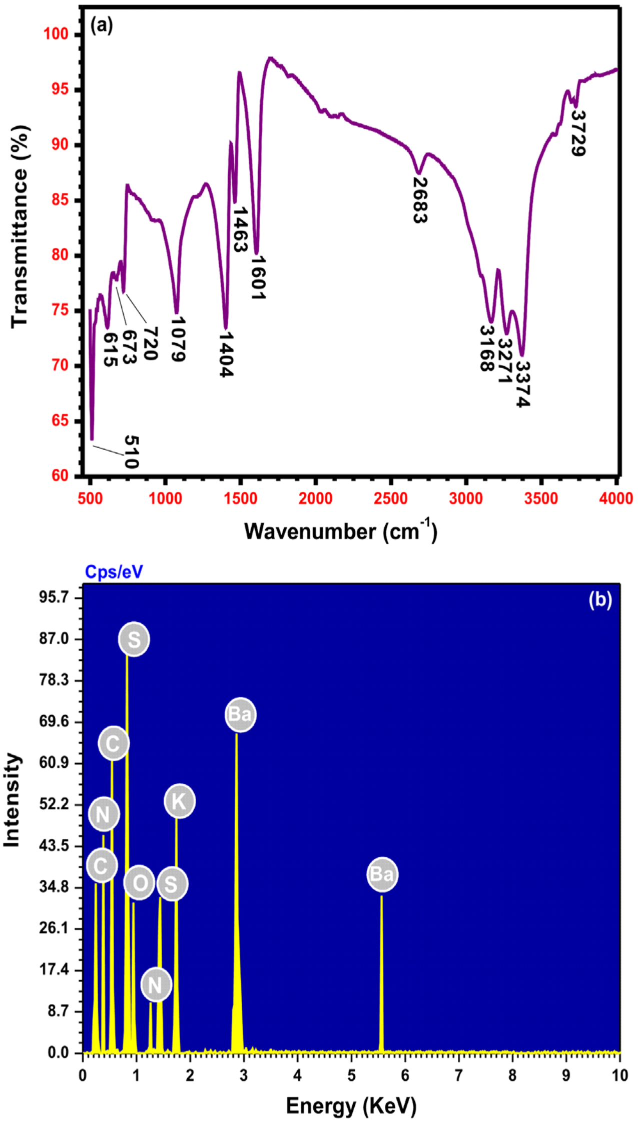

Figure 2. (a) FT-IR spectrum of TTPBS crystal and (b) EDS spectrum of TTPBS.

the requirements necessary for designing optical components for transmission of second/third harmonic signals of 1064 nm lasers and UV–tunable laser devices [36].

The asymmetry in crystal structure is the key factor responsible for frequency doubling phenomenon which can be identified by the standard Kurtz-Perry test [37]. For present investigation the powder sample of identical size of TTPBS crystal were prepared and tightly sieved in the quartz micro-capillary tube of uniform bore. The Gaussian filtered beam of Nd:YAG laser (1064 nm, 6 ns, 10 Hz) operating in Q-switched mode was multishot on the sample placed in the optical path and the output of the sample was finally collected as an electrical signal displayed on digital oscilloscope. The output contributed by KDP and TTPBS crystal is 75 and 57 mV respectively. The SHG efficiency of TTPBS crystal is thus found to be 76% of that of KDP crystal material. The powder sample of thiourea crystal did not show second order NLO behavior owing to centrosymmetric structure [38]. However in present studies the coordination of thiourea with metal ions results to formation a new noncentrosymmetric complex crystal TTPBS which is responsible for observed SHG response. Thus the TTPBS crystal could be utilized for constructing frequency doubler/convertor devices [39].

The Z-scan is the most sensitive technique designed by Bahae et al. [40] to analyze the optical nonlinearities fostering due to irradiation of laser beam of particular wavelength propagating with high frequency. The optical resolution of He–Ne laser assisted Z-scan setup is detailed in Table 2. In current investigation the TTPBS crystal sample was polished and placed at the focus position ($Z = 0$) of beam irradiated optical path. The optical path i.e. Z-direction is divided in two equal lengths ranging from −15 to 15 mm. The analysis was started by focusing the Gaussian filtered beam on the crystal samples using the converging lens and the crystal was gradually translated along the *Z*-direction. For closed aperture Z-scan analysis the optical path dependent intensity transmitted through the crystal sample was recorded using the photo detector with closed aperture placed at far field. The close aperture Z-scan transmittance curve is depicted in Figure 4(a) which reveals that the grown crystal attributes the nonlinear refraction (n_2) of positive signature which is identity feature of material demonstrating self-focusing nature [41]. The phase shift in intensity of n_2 about the focus is originated due to localized thermal lensing effect causing the spacial distribution of the energy along the crystal surface [42]. In addition the repetition rate and intensity of laser beam at the focus are the decisive parameters that can tune the n_2 of given material [43]. The peak to valley transmission (ΔT_{p-v}) can be expressed in phase shift as give below [40],

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25}|\Delta\phi| \tag{1}$$

where $S = [1 - \exp(-2r_a^2/\omega_a^2)]$ is the aperture linear transmittance, r_a is the aperture radius and ω_a is the beam waist radius in front of aperture. The n_2 of crystals has been determined using the relation [40],

$$n_2 = \frac{\Delta\phi}{KI_0L_{eff}} \tag{2}$$

where $K = 2\pi/\lambda$, I_0 is the incident irradiance intensity of beam at the focus (Z = 0), the effective thickness of the sample $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$ where, α is the linear absorption coefficient and L is the thickness of the sample. The positive n_2 of magnitude 4.41×10^{-11} cm^2/W suggest the prominence of kerr lens modelocking (KLM) ability in TTPBS crystal which is essential to be utilized in continuous-wave mode-locked lasers and shorter pulse generation system [44,45]. The presence of nonlinear absorption in grown crystal can be identified using the open aperture Z-scan configuration and the open aperture Z-scan curve is shown in Figure 4(b). It reveals that transmitted intensity becomes minimum when the crystal is moved towards the focus and becomes high when translated away from the focus. This indicates the presence of reverse saturable absorption (RSA) effect [46]. The RSA effect is facilitated by multi-photon absorption (MPA) phenomenon assisted with excited state absorption (ESA) confirming the population dominance in cross sectional area of excited states relative to ground states [47,48]. The β value has been calculated using equation [40],

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{eff}} \tag{3}$$

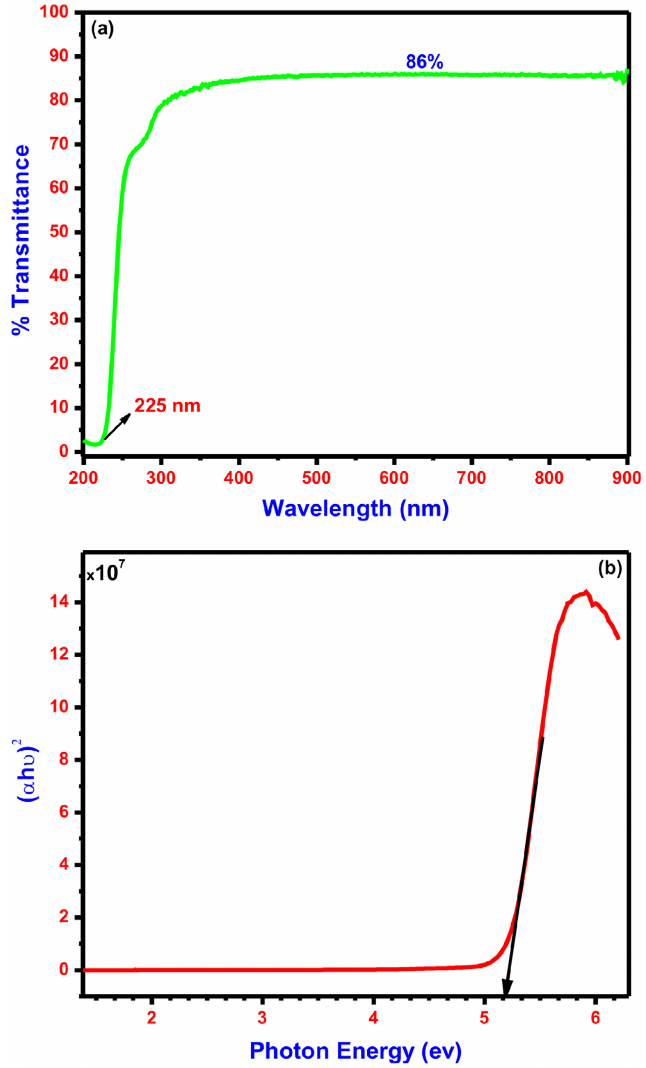

Figure 3. (a) Transmittance spectrum and (b) Tauc's plot.

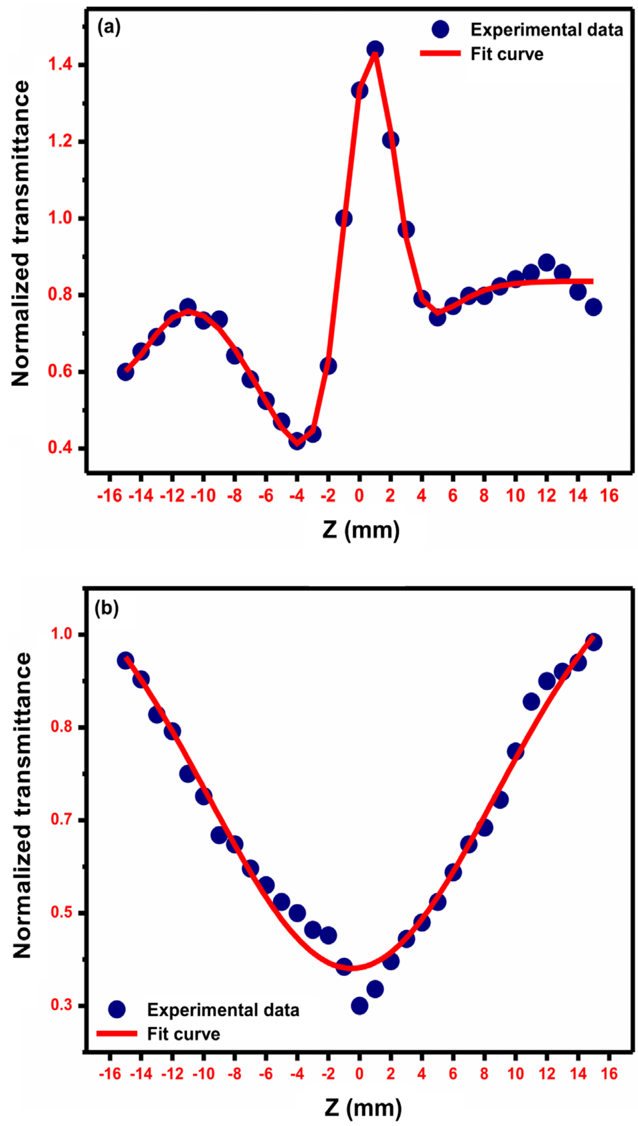

Figure 4. Z-scan transmittance curve with aperture (a) close and (b) open.

Table 2. Optical resolution of Z-scan setup.

Parameters and notations	Details
Laser wavelength (λ)	632.8 nm
Lens focal length (f)	30 mm
Optical path distance (Z)	85 cm
Beam waist radius (ω_a)	3.3 mm
Aperture radius (r_a)	2 mm
Incident intensity at the focus (I_o)	5 MW/cm^2

Table 3. Optical properties of TTPBS crystal.

Parameter	Magnitude
Cutoff wavelength	225 nm
Band gap	5.16 eV
Transmittance	86%
SHG efficiency	76% of that of KDP
LDT at 1064 nm	3872.61 MW/cm^2
n_2	4.41×10^{-11} cm^2/W
β	1.10×10^{-6} cm/W
χ^3	3.44×10^{-6} esu

where ΔT is the one valley value obtained in open aperture Z-scan curve. The nonlinear absorption coefficient (β) of TTPBS crystal is thus found to be 1.10×10^{-6} cm/W. The cubic susceptibity (χ^3) of grown crystal has been analyzed by solving the following equations [40],

$$\mathrm{Re}\chi^{(3)}(\mathrm{esu}) = 10^{-4}(\varepsilon_0 C^2 n_0^2 n_2)/\pi(\mathrm{cm}^2/\mathrm{W}) \quad (4)$$

$$\mathrm{Im}\chi^{(3)}(\mathrm{esu}) = 10^{-2}(\varepsilon_0 C^2 n_0^2 \lambda\beta)/4\pi^2(\mathrm{cm}/\mathrm{W}) \quad (5)$$

$$\chi^3 = \sqrt{(\mathrm{Re}\chi^3)^2 + (\mathrm{Im}\chi^3)^2} \quad (6)$$

where ε_0 is the vacuum permittivity, n_0 is the linear refractive index of the sample and C is the velocity of light in vacuum. The TTPBS crystal has a high magnitude of χ^3 of magnitude 3.44×10^{-6} esu which dwells due to photoinduced π-electron delocalization along wide bonding network resulting to strong polarizing potential in crystal [49]. The material with promising TONLO properties thus seek much utility in field of two-photon upconversion lasing, optical switching, optical limiting, 3D optical data storage, photodynamic therapy, lithography microscopic fabrication, fluorescence excitation microscopy and imaging [50,51].

The NLO crystals with ability to withstand high laser power shots for longer duration are largely demanded for photonic device applications and therefore the TTPBS crystal has been subjected to laser damage threshold (LDT) analysis using the Q-switched mode operated Nd:YAG laser (pulse mode, 1064 nm, 10 ns, 10 Hz). The TTPBS crystal was finely polished and placed at the sample holder.

The polarized laser beam was focused on the TTPBS crystal through the converging lens of focal length 35 cm. The energy of the incident laser beam was attenuated and the impact of laser shot was observed for each energy shot. The TTPBS crystal eventually showed a major damage at incident beam energy of 304 mJ. It is known that the surface laser damage is rather a complex phenomenon which originates due to simultaneously evolved effect (electron avalanche, multi photon absorption and thermally contributed localized photo-ionization of crystal material) [52,53]. However, at nanosecond pulse scale the photo-ionization due to thermal conduction is more dominant phenomenon which is also the reason for LDT in TTPBS crystal. The LDT of TTPBS crystal was calculated using the relation $P = E/\tau\pi r^2$ and it is found to be 3872.61 MW/cm^2. The LDT value of TTPBS crystal is sufficiently higher than crystals such as bis-thiourea zinc acetate (12.44 MW/cm^2), potassium dihydrogen orthophosphate (0.2 MW/cm^2), benzimidazole (1.9 MW/cm^2) [54] and Cu-ZTC (706.2 MW/cm^2) [55]. In addition the investigated optical properties of TTPBS crystal are integrated in Table 3.

4. Conclusion

In present studies the TTPBS crystal has been successfully grown by slow solvent evaporation technique. The functional groups of thiourea present in TTPBS crystal is confirmed by FTIR analysis and the EDS analysis confirmed the presence of metal ions potassium and barium. The single crystal XRD analysis confirmed the orthorhombic structure of TTPBS crystal. The linear and nonlinear optical properties of TTPBS crystal have been explored by UV–visible, Kurtz-Perry test, Z-scan and LDT analysis. The TTPBS crystal offers uniform optical transmittance of 86%, low cutoff wavelength of 225 nm and wide optical band gap of 5.16 eV. The nonlinear behavior of TTPBS crystal has been confirmed by Kurtz-Perry test and the Z-scan analysis. The TTPBS crystal delivered the SHG efficiency 76% of that of KDP crystal material which also confirms its noncentrosymmetric symmetry. The TTPBS crystal contributed positive refraction nonlinearity and reverse saturable absorption at 632.8 nm. The magnitude of n_2, β and χ^3 of grown crystal is found to be 4.41×10^{-11} cm^2/W, 1.10×10^{-6} cm/W and 3.44×10^{-6} esu respectively. The LDT of TTPBS crystal determined at 1064 nm is found to be 3872.61 MW/cm^2. The TTPBS crystal with excellent linear and nonlinear optical properties could be suitable candidate for designing optical limiting, frequency conversion, optical switching, 3D optical data storage and photonic devices.

Highlights/Novelty Factors

- New tris thiourea potassium barium sulphate (TTPBS) crystal is grown
- Transmittance, cut-off wavelength and band gap of TTPBS crystal is 86%, 225 nm and 5.16 eV
- At 632.8 nm TTPBS crystal offers + ve refraction nonlinearity and reverse saturable absorption effect
- The n_2, β and χ^3 of TTPBS crystal is of order 10^{-11} cm^2/W, 10^{-6} cm/W and 10^{-6} esu
- The 1064 nm Nd:YAG laser induced LDT of TTPBS crystal is 3872.61 MW/cm^2

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Disclosure statement

No potential conflict of interest was reported by the authors.

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Notes on contributors

SM Azhar, G Rabbani, MD Shirsat, SS Hussaini, Mohd Anis conceived and designed the study. Mohd Anis, MI Baig, Mohd Shkir analysed the data, wrote the article in whole/part and revised the article. S Alfaify, HA Ghramh collected and partly analysed the data.

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