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Crystal growth, spectral, structural and optical studies of π -conjugated stilbazolium crystal: 4-Bromobenzaldehyde-4'-N'-methylstilbazolium tosylate



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HIGHLIGHTS

- The morphology of the BMST crystal was depicted using WinXMorph program.
- FT-IR, FT-Raman and ¹H NMR assignments confirmed the functional groups of BMST.
- Bond length alternation value was found to be 0.086 Å.
- Band gap energy and refractive index were found to be 2.96 eV and 2.41 respectively.
- Kurtz powder test confirmed that SHG intensity increases with increase in particle size.

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ABSTRACT

Nonlinear optical (NLO) organic compound, 4-bromobenzaldehyde-4'-N'-methylstilbazolium tosylate was synthesized by reflux method. The formation of molecular complex was confirmed from ¹H NMR, FT-IR and FT-Raman spectral analyses. The single crystals were grown by slow evaporation solution growth method and the crystal structure and atomic packing of grown crystal was identified. The morphology and growth axis of grown crystal were determined. The crystal perfection was analyzed using high resolution X-ray diffraction study on (001) plane. Thermal stability, decomposition stages and melting point of the grown crystal were analyzed. The optical absorption coefficient (α) and energy band gap (E_g) of the crystal were determined using UV–visible absorption studies. Second harmonic generation efficiency of the grown crystal was examined by Kurtz powder method with different particle size using 1064 nm laser. Laser induced damage threshold study was carried out for the grown crystal using Nd:YAG laser.

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Introduction

Recent years, molecular-based second-order nonlinear optical crystals have attracted much interest because of their potential applications in emerging optoelectronic technologies [1,2]. These

http://dx.doi.org/10.1016/j.saa.2014.01.029 1386-1425/© 2014 Elsevier B.V. All rights reserved. efforts have mainly focused on organic systems [3]. The design of new organic compounds with large nonlinear optical polarizabilities is of crucial importance [4]. Much efforts have been made to develop new materials with high second-order nonlinearities and are expected to underpin applications in the areas such as electro-optic switching for telecommunications [5], optical information processing [6], optical data storage [7,8], and the generation of terahertz radiation [9]. Among the various classes of materials

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investigated worldwide, ionic organic NLO crystals are of special interest due to their advantageous in mechanical, chemical and thermal properties [10]. Organic crystal 4-N,N-dimethylamino-4',N'-methylstilbazolium tosylate (DAST) is one of the most widely used NLO materials, showing large NLO susceptibility, $d_{11} = 1010 \pm 110 \text{ pm/V}$ at 1318 nm, and large electro-optic coefficient, $r_{11} = 50 \pm 5 \text{ pm/V}$ at 1313 nm. It also has a lower dielectric constant, $\varepsilon_{11} = 5.2$ than standard NLO crystals [11,12].

To improve the second-order NLO response of ionic organic crystals, a number of approaches have been demonstrated in recent years. Also its high potential for the above applications encourages the development of new DAST derivative crystals by varying the counter anion and cation structure [3]. Furthermore, Duan et al. shown that the electron-donating strength of the donor unit in a series of stilbazolium salts increased (via CN, Br, Cl, H, CH₃, CHCl₃, OCH₃ or OH substitution) the quadratic NLO (β) value of compound [13]. Mardar et al. reported that the second-order harmonic generation efficiency of the title compound 4-bromobenzal-dehyde-4'-N'-methylstilbazolium tosylate (BMST) is five times than Urea at 1064 nm radiation [14].

The aim of the present work is to synthesis, crystal growth and its different characterization for better understanding of properties of the title compound. It crystallizes in $P2_1/c$ space group of monoclinic system and also it possesses good second harmonic generation (SHG) property [15]. In the present report, the infrared, Raman, ¹H NMR spectra of the compound were recorded and elemental analysis was carried out to analyze the formation of the compound. The UV–visible transmission, Kurtz powder SHG and photoluminescence properties have been studied to understand the optical behavior. Furthermore, the structure, morphology, crystal perfection and thermal properties of title compound have also been studied.

Experimental procedure

Material synthesis

All the starting materials with high purity (Aldrich) were used to synthesis 4-bromobenzaldehyde-4'-N'-methylstilbazolium tosylate compound by Knoevenagel condensation reaction [16] by using Dean–Stark apparatus (Fig. 1). Knoevenagel reaction is generally carried out in the presence of weak bases such as piperidine and ethylene-diamine. This condensation is important for vinyl carbon–carbon (C=C) double bond-forming reaction in water [17]. The round-bottomed flask equipped with condensation setup was used for the synthesis. The steps involved during chemical reaction are as follows: The



Fig. 2. Solubility and nucleation curves of BMST in methanol solvent.

equimolar quantity of reagents was used. The measured 4-picoline (0.105 mol%) and methyl p-toluenesulfonate (0.105 mol%) were added to 200 ml of toluene in the round bottom flask. It was refluxed by applying heat, until it crystallizes as intermediate white salt, which is insoluble in toluene. It was dissolved by adding 200 ml of N,Ndimethylformamide (DMF) into the solution. After getting the clear solution. 4-bromobenzaldehvde (0.105 mol%) was added slowly to the solution. In addition, few drops of piperidine were added into the solution and the solution color was changed into orange immediately. The solution was refluxed for 20 h using Dean-Stark trap to remove water. Then, the solution was cooled to room temperature and the orange colored BMST precipitate was collected from the round bottom flask. Then, the salt was dried in the hot air oven at 100 °C for an hour. The CHN elemental analysis was done to explore the composition of the synthesized compound. The composition of synthesized compound with chemical formula, C₂₁H₂₀BrNO₃S; was calculated as C, 56.45%; H, 4.48%; N, 3.09%. These values are agreed very well with the estimated values. The CHN analysis confirmed that, the synthesized salt is 4-bromobenzaldehyde-4'-N'-methylstilbazolium tosylate. The purity of the salt was improved by repeated recrystallization process in methanol at least five times and was used for crystal growth.

Crystal growth

The single crystals of 4-bromobenzaldehyde-4'-N'-methylstilbazolium tosylate were grown by slow evaporation method



Fig. 1. Knoevenagel condensation reaction for BMST compound.



Fig. 3. (a) Photograph of as-grown BMST single crystals. (b) Equilibrium morphology of BMST single crystal.

[18]. The solubility of BMST salt in methanol was determined experimentally. The solubility and nucleation curves of BMST are presented in Fig. 2. Based on the solubility data, the saturated growth solution at 40 °C was prepared by continues stirring of about 6 h. The pure solution was obtained by filtration and transferred to Teflon container to avoid sticking of the salt on the wall. The beaker was sealed with perforated cover and kept at 40 °C (±0.01 °C) using constant temperature bath. The solution was allowed for slow evaporation. After the evaporation period of three weeks, the spontaneous nucleation was occurred in the supersaturated solution and the developed crystals were collected. The collected as-grown BMST single crystals with size up to $9 \times 3 \times 3 \text{ mm}^3$ are shown in Fig. 3a. Its equilibrium morphology was obtained using WinXMorph program and it is shown in Fig. 3b.

Results and discussion

Spectral studies

Infrared and Raman spectral analyses

The infrared (IR) and Raman spectra were recorded using JASCO FTIR 410 spectrometer $(4000-450 \text{ cm}^{-1})$ and Bruker RFS27 $(4000-50 \text{ cm}^{-1})$ with 100 mW laser excitation respectively. KBr pellet technique was used for infrared spectrum. These vibrational methods can provide valuable information about the force field of the molecules and can help to understand the chemical and physical properties in solid state. The vibrational spectral analysis was performed on the basis of the characteristic vibrations of stilbazo-lium cation and toluene sulfonate anion. Figs. 4 and 5 are the

experimental infrared and Raman spectra of the BMST compound. It is observed that all the vibrational bands are asymmetric. It suggested that, electron interaction between the strongest neutral donor p-bromobenzaldehyde, methyl p-toluenesulfonate and the strongest acceptor group of pyridine. The measured infrared and Raman band positions and their assignments are given in Table 1.

Stilbazolium cation group vibrations

Vinyl group vibrations

The vibrations of ethylenic bridge (C=C) are highly sensitive to degree of charge transfer between the donor and acceptor groups and hence such stretching modes are of particular interest for spectroscopists [19,20]. Two characteristic vibrational bands at 1644 and 1585 cm⁻¹ occurred in IR spectrum are due to π -conjugated C=C ethylenic group. The downshift of the C=C stretching wavenumber reveals that the vinyl group is actively involved in the conjugation path. One is most localized on the aromatic donor (pbromobenzaldehyde) fragment and the other on the pyridine acceptor (p-picoline) fragment. For each pair of related vibrations, the pyridine component is occurred at lower wavenumber in the π -conjugated molecules. This observation implies that the π -conjugation between the vinyl group and benzene ring mainly changes the bond length alternation (BLA) of the vinyl group C=C and C-C bonds. It is key parameter for second harmonic generation property of centrosymmetric crystals. The characteristic vibrations of vinyl aliphatic C-H stretching are expected between 3050 and 3000 cm^{-1} for stilbazole derivatives [21]. The C₇-H and C₈-H stretching modes are appeared at 3049 cm⁻¹ in infrared spectrum. The in-plane and out-of plane deformation vibration bands of aliphatic C–H group are observed at 1195, 942 cm⁻¹ in infrared and at 1183 cm⁻¹ in Raman spectra.

Phenyl and pyridine ring vibrations

The ring vibrational modes of cationic group of BMST were analyzed on the basis of stilbazolium ring, which consists of p-bromine substituted benzene and pyridine moieties connected by ethylenic bridge. The vibrational modes of pyridine component of BMST are very similar to those of benzene and it derivatives. The ring stretching vibrations are prominent in the infrared spectrum of p-substituted benzene ring complexes. The substitution of ethylenic bridge does not perturb much on C—C bond lengths



Fig. 4. FT-IR spectrum of BMST compound.



Fig. 5. FT-Raman spectrum of BMST compound.

Table 1

Infrared and Raman band positions (cm⁻¹) and their assignments of BMST.

v_{IR} (cm ⁻¹)	v_{Raman} (cm ⁻¹)	Assignments
3168 m	-	Ring II v (C—H)
3128 m	3069 vs	Ring I v (C-H)
3090 w	-	Ring III v (C-H)
3049 s	-	Vinyl C–H stretching
2965 w	-	CH ₃ group of ring III asymmetric stretching
2918 w	-	CH ₃ asymmetric stretching
2861 w	-	CH ₃ group of ring III symmetric stretching
1644 m	-	υ (C ₇ =C ₈)/vinyl C-H rocking
1624 vvs	-	υ (C ₇ =C ₈)/ring υ (C=C)
1585 vs	-	υ (C=C)/υ (C-C)
1519 ssh	1564 w, 1520 w	Ring υ (C=C)
1488 m	1478 vw	CH ₃ asymmetric deformation
1473 m	-	Ring v (C=C)
1404 m	1404 w	Ring v (C=C)
1331 s	1349 vw, 1332 w	CH ₃ symmetric deformation
1220 s	1286 w, 1208 w	Ring δ (C—H)
1195 s	1183 s	Vinyl C—H bending/va (SO ₂)
1122 s	-	Ring δ (C—H)
1104 w	-	Ring δ (C—H)
1073 m	1073 w	CH ₃ rocking
1032 s	-	Ring δ (C—H)
1010 s	1010 vw	Ring δ (C—H)
979 w	-	Ring δ (C—H)
942 w	-	Vinyl υ (C—H)
884 s	884 w	Ring δ (C—H)/C—N stretch
837 s	-	Ring δ (C—H)
821 s	-	Ring v (C—H)
807 w	802 w	Ring v (C—H)
772 w	772 w	Ring δ (CCC)
713 w	-	Ring v (CCC)
680 vvs	-	Ring v (CCC)
563 s	-	CH ₃ twisting
534 s	-	C—Br stretching
-	308 vw	CH ₃ torsion/C—Br stretching
-	288 vw	Ring torsion/C—Br bending
-	68 w	Tosylate vibrations

Abbreviations: υ – stretching vibration; δ – deformation vibration; m – medium; w – weak; s – strong; vs – very strong; vvs – very very strong.

 $(C_4-C_7 = 1.465 \text{ Å}, C_8-C_9 = 1.470 \text{ Å})$ with benzene rings. The C--H vibrations of p-bromo phenyl ring are observed at 3128, 3049 and 3069 cm⁻¹ in infrared and Raman spectra respectively and also it agrees with previous reported assignments [22]. The symmetric and asymmetric stretching vibrations in each pair of C--H bonds in the bromobenzene (ring I) have very near frequency vibrations. The band at the higher wavenumber can be assigned to two overlapping modes arising from the mixed C₂--H and C₆--H stretching

vibrations of C–H bonds in ortho-position and the C₁–Br bond. The band at the lower wavenumber in this region arises from the mixed stretching vibrations of two C–H bonds (C_3 –H and C_5 –H) in the ortho-position of the vinyl group (C–C). Similarly, the ring C-H stretching vibrations is appeared at 3168 (pyridine - ring II) and 3090 cm⁻¹ (methyl p-toluenesulfonate – ring III) vibrations in the IR spectrum. The C-H in-plane bending character can be expected in the region 1300–1000 cm⁻¹. The C–H in-plane deformation ring characteristic vibrations are occurred at 1195 cm⁻¹ in IR spectrum and at 1208, 1183 cm⁻¹ in Raman spectrum. Furthermore, such deformation changes the bond length between the carbon atoms and the polarizability of such π -conjugated system. The ring mode vibration is occurred at 1220 cm^{-1} in the IR spectrum as an intense band. The C-H out-of-plane bending vibrations of phenyl ring are usually observed in the region 1000–675 cm⁻¹. The C–H out-of-plane vibrations are observed as strong bands at 884 and 884 cm⁻¹ in IR and Raman spectrum respectively, and also a weak band is appeared at 837 cm^{-1} in IR spectrum. The existence of phenyl ring modes at 713, 680 and 534 cm⁻¹ in IR spectrum, clearly indicates that the BMST chromophore is non-polar [23].

Halogen (C-Br) group vibrations

In the Raman spectrum of BMST, the stretching vibration of bromine (υ ; C—Br) contributes to the bands observed at 288 and 1073 cm⁻¹. Also the υ (C—Br) out-of-plane bending vibrations are occurred at 308 cm⁻¹. These results show very good agreement with the earlier report for p-bromo substituted aniline and phenol [24]. It confirms the presence of bromine atom in the synthesized complex.

Methyl group vibrations

Methyl groups are referred to as an electron donating substituent in the aromatic ring system [25]. Two kinds of methyl groups are present in the BMST molecule, one type N–CH₃ attached with pyridine ring and other type is C-CH₃ of tosylate anion. The C-H stretching vibrations of the methyl group usually occurs in the region 3000-2840 cm⁻¹. It is observed that weak bands at 2965, 2918 cm⁻¹ in IR spectrum are referred to C—H stretching of methyl group in pyridine ring and tosylate anion. The asymmetrical bending vibrations δ_{as} (CH_3) and symmetrical bending vibrations δ_s (CH_3) of methyl groups are occurred near 1450 and 1375 cm $^{-1}$ respectively. The asymmetrical bending vibrations are appeared in the IR spectrum at 1473 cm⁻¹, while vibrations at 1331 cm⁻¹ in IR spectrum and 1349, 1332 cm^{-1} in Raman spectrum are due to symmetrical bendings of CH₃ group. The rocking mode of the CH_3 groups generally lies between the region 1070–1010 cm⁻¹ and it is observed at 1073 cm⁻¹ in infrared and Raman spectra. The twisting and torsion of methyl group vibrations are found at 563 cm^{-1} in IR and 308, 288 cm^{-1} in Raman spectra.

Sulfonate group and skeletal vibrations

The sulfonate functional groups contain the SO₂ group and it gives rise to strong IR bands between $1450-1150 \text{ cm}^{-1}$ for symmetric and asymmetric stretching vibrations. The sulfonate group contains one S–O bond and two S=O bond stretches and it appeared in the region $1430-1330 \text{ cm}^{-1}$ [26]. The sulfonate group vibrations are observed at 1195 cm^{-1} in IR and 1183 cm^{-1} in Raman spectra. The symmetric stretching vibrations of SO₂ group are identified at 1032 cm^{-1} in IR and at 1073 cm^{-1} in the Raman spectra. The skeletal vibration bands rise from C–C and C–N stretching are generally measured in the region $1150-850 \text{ cm}^{-1}$. The skeletal mode vibrations are observed at 884 cm^{-1} both in

the IR and Raman spectra and it is assigned to C–N stretching mode.

¹H NMR spectral studies

The ¹H NMR spectrum provides information about the number of different types of protons and also the nature of the immediate environment of each of them. The BMST compound consists of different types of hydrogen attached with others in the molecular structure. ¹H NMR spectrum of BMST was recorded in deuterated methanol (MeOD) and is presented in Fig. 6a and b. It shows different chemical shifts δ through absorption peaks with respect to its chemical environment in the molecule. The doublet chemical shift ' δ ' at 8.7 ppm is due to two (C–H) hydrogen atoms present in the pyridine (ring II), and it is neighbor of (N–C) bond. The rest of two hydrogen atoms in the pyridine ring raised the doublet chemical shift ' δ ' at 8.14 ppm. Also the chemical shift of hydrogens in methyl (N–CH₃) group attached with pyridine ring gives ' δ ' at 4.32 ppm. The two doublets chemical shifts observed ' δ ' at



Fig. 6. (a) ¹H NMR spectrum of BMST in MeOD. (b) ¹H NMR spectrum of BMST in MeOD.

7.62 ppm and 7.66 ppm are due to the hydrogen atoms of p-bromobenzene (ring I) of the compound. The first doublet represents the hydrogen atom which is neighbor of bromine (Br–C–C–H) chemical environment and second is due to the rest of two hydrogens. The chemical shifts of two doublets of (C–H) at 7.23 ppm and 7.42 ppm are due to the ring hydrogens of methyl p-toluenesulfonate (ring III). The singlet chemical shift 'δ' at 2.36 is due to the methyl (CH₃) group hydrogens in ring III. All the observed chemical shifts of ¹H NMR spectra clearly confirmed that, all hydrogen atoms with respective environment are present in molecular structure of the complex.

X-ray diffraction studies

Single crystal X-ray diffraction study

The crystal structure of grown 4-bromobenzaldehyde-4'-N'methylstilbazolium tosylate single crystal was determined using Bruker Kappa APEX II diffractometer. Mo K_α radiation with wavelength of λ = 0.71073 nm from graphite monochromator was used for recording the reflections. The collected data was solved using WINGX programme and structure was refined by a direct method using SHELXL-97. The refined crystal structure with 'R' factor 0.0428 revealed that, crystal belongs to monoclinic system with

Table 2

Crystal structure data of BMST.

Parameters	Crystal data
Molecular formula Molecular weight Crystal system Space group Point group symmetry Hall symbol	C ₂₁ H ₂₀ BrNO ₃ S 446.35 g/mol Monoclinic P2 ₁ /c 2/m -P2ybc
Unit cell dimensions	a = 9.0502(2) Å; b = 6.4201(1) Å; c = 33.9280(7) Å; $\alpha = \gamma = 90^{\circ}, \beta = 94.469(1)^{\circ}$ V = 1965.33 Å ³

the space group of $P2_1/c$. The hall symbol of the system is -P2ybcand the unit cell contains four ion-pairs (Z = 4). The estimated cell parameters of the grown crystal are given in Table 2. From the OR-TEP diagram (Fig. 7) of the molecule, it is observed that the two independent molecules, C14H13BrN and C7H7O3S are stabilized in weak C—H—O interactions and forming asymmetric unit. The ring I (p-bromobenzaldehyde) attached with ring II (p-picoline) via strong vinyl C=C bond and its dihedral angle is 8.4(2)°. The torsion angle between C4–C7 and C8–C9 is 178.1(3)°. The disorder in bromine atom positions and disordered over two positions with site occupancies of 0.72(3) and 0.28(3) was observed in ring I. The disorder in crystal structure contributes a sizable magnetic dipole and an electric quadrupole moment to the bulk susceptibility [27–30], which is responsible for second harmonic generation property. In addition, bond length alternation (BLA) is found to be 0.086 Å, which is the difference between average bond distances of single and double bonds of carbon in the molecule [31,32]. The magnitude of BLA is a useful indicator of second-order NLO response and compounds with BLA values approximately ±0.05 Å are expected to exhibit the greatest NLO responses, while compounds with BLA value zero are anticipated to exhibit no second-order NLO response [33]. Some of the selected bond lengths of the crystal are given in Table 3. The crystal structural analysis revealed that, the structural key parameter BLA and observed disorder may be the reason for observing second-order NLO property from BMST compound.

It is useful to know the relation between morphological variations and the growth parameters which extends to applied fields including metal solidification, quality control of optoelectronic crystals and industrial crystallization. The morphology of BMST crystal was predicted using WinXMorph program [34,35] and it is depicted in Fig. 3b. The morphology of BMST revealed the well developed ten facets such as (100), $(\bar{1}00)$, $|(0\bar{2}\bar{3})$, $(\bar{1}\bar{2}\bar{3})$, $(0\bar{2}3)$, (123), $(02\bar{3})$, $(1\bar{2}3)$, $(0\bar{2}3)$, $(\bar{1}2\bar{3})$. The morphology of the grown crystal (Fig. 3b) shows that, (100) and $(\bar{1}00)$ facets have larger surface area than other facets. The angle between the facets (100)– $(0\bar{2}3)$, $(100)–(1\bar{2}3)$ and $(1\bar{2}3)–(0\bar{2}3)$ of grown crystal found from morphology are 91.223°, 70.019° and 18.759° respectively. Hence, the morphology of BMST crystal suggests that,



Fig. 7. Molecular ORTEP diagram of BMST crystal.

Table 3	
Selected bond lengths and magnitude of BLA ((Å) for BMST.

Bond	Distances (Å)
C-Br1 C-Br1 [*] C4-C7 C7-C8 C8-C9 C18-C21	$1.878(4) \\ 1.924(9) \\ 1.466(4) \\ 1.304(4) \\ 1.468(4) \\ 1.510(5) \\ 0.9950$
DLA	0.086

(100) and $(\bar{1}00)$ planes are the suitable facets for device applications.

High resolution X-ray diffraction (HRXRD) study

The crystalline perfection of the BMST single crystal was characterized by HRXRD using multicrystal X-ray diffractometer [36]. A well-collimated and monochromated Mo $K_{\alpha 1}$ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration was used as the exploring X-ray beam. The specimen crystal of BMST was aligned in the (+, -, -, +) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The rocking or diffraction curves were recorded by changing the glancing angle around the Bragg diffraction peak position $\theta_{\rm B}$ starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak, so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve. The DC was recorded by the so called ω scan wherein, the detector was kept at the same angular position $2\theta_{\rm B}$ with wide opening for its slit. This arrangement is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries [37,38]. Before recording the diffraction curve, the non-crystallized solute atoms remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces of grown crystals by solution methods can be removed [39]. Also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non-preferential etchant.

Fig. 8 shows the recorded HRXRD curve on (100) diffraction plane for a typical BMST single crystal specimen. On close observation, one can realize that the curve is not a single peak. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks. The solid line of convoluted curve is well fitted with the experimental points represented by the filled circles, which are 70 and 125 arc sec. away from the main peak on both the sides. These two additional peaks correspond to two internal structural low angle boundaries with tilt angle >1 arc min. but <1 degree boundaries [40]. The tilt angle may be defined as the misorientation angles between the two crystalline regions on both sides of the structural grain boundary are 70 and 125 arc sec. from their adjoining regions. The full width at half maximum (FWHM) of the main peak and the two very low angle boundaries are respectively 68 and 138 and 145 arc sec. The relatively low values of FWHM of the grains in comparison with that of the real life crystals are depicts that the crystalline perfection is fairly good. It may be mentioned here that such low angle boundaries could be detected in the diffraction curve only because of the high-resolution of the diffractometer used in the present investigations. The presence of such defects may not influence much on the NLO properties.



Fig. 8. HRXRD rocking curve of BMST single crystal on (100) plane.

However, a quantitative analysis of such unavoidable defects is of great importance, particularly in case of phase matching applications [41].

Optical characterization

UV-visible study

The optical properties of the grown crystal were studied by recording UV–visible spectrum using SHIMADZU 1800 UV–visible spectrophotometer. UV–visible transmittance spectrum was recorded in the range 200–800 nm (Fig. 9). It is very useful to identify the optical absorption or transmission window and cut-off wavelength of the crystal. Also it is useful to understand its electronic states, when interacting with linear light. Absorption of ultraviolet and visible light involves the promotion of the electrons in σ - and π -orbitals from the ground state to excited energy states [42]. The BMST crystal was transparent from 419 nm to 900 nm and below 419 nm wavelength, the crystal was opaque. From the spectrum, it is evident that the BMST crystal has optical cut-off at 419 nm and found no absorption in the most visible region, which is needed quality of a crystal for optical applications.

Optical constants estimation

The optical constants of the materials are important parameters for the fabrication of optical devices. The estimation of energy band gap (E_g) and refractive index (n_1) of a specific material are the essential criteria for linear and nonlinear optical applications. The energy band gap of the material is very closely related to the atomic structure and electronic band structure of the materials [43]. The energy band gap (E_g) of the material is very closely related to the materials with atomic and electronic band structures. The band gap energy was calculated using the relation,

$$E_{\rm g} = hc/\lambda \tag{1}$$

where *h* is the Planck constant, *c* is the velocity of light and λ is the cut-off wavelength of the crystal. Hence, the band-gap energy of the grown crystal was estimated to be 2.96 eV.

Typically, main optical parameters of the grown crystal are absorption coefficient (α) and refractive index (n). The optical absorption coefficient (α) of BMST crystal at different wavelengths was calculated using Eq. (1) [44].

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \tag{2}$$

where T is the transmittance and t is the thickness of the sample used for this study. A typical relationship between absorption



Fig. 9. UV-visible transmittance spectrum of BMST crystal.

coefficient and the photon energy observed in the crystal is presented in Fig. 10. From the spectrum, all the possible absorption and electronic processes were studied. It is due to the possible electronic transitions at the molecular levels. Free carrier absorption is due to the presence of free electrons and holes and that decreases with increase in photon energy. There was no absorption band due to presence of impurities in the compound. The lattice absorption is due to the radiation absorbed by vibrations of the crystal ions (Fig. 10). The fundamental absorption of photons is observed in the region of 5.09 eV and due to band-to-band excitation, in which an electron can move from the valence to the conduction band. It is observed from the spectrum that, it has large absorption coefficient and it is occurred, when the photon energy reaches the bandgap energy. The maximum absorption is noticed at the lower energy. which is below 419 nm and $\pi - \pi^*$ energy transition takes place in this region, when the applied energy reached the higher energy value of about 2.96 eV in terms of light.

The refractive index of the optical material can be calculated using transmission spectrum of the crystal and the reflectance of the crystal in terms of absorption coefficient was calculated using Eq. (3),

$$R = 1 \pm \frac{\sqrt{1 - \exp(-\alpha t) + \exp(\alpha t)}}{1 - \exp(-\alpha t)}$$
(3)



Fig. 10. Plot of absorption coefficient (α) vs. photon energy of BMST crystal.

$$n = \frac{-(R+1) \pm \sqrt{-3R^2 + 10R - 3}}{2(R-1)} \tag{4}$$

The linear refractive index (n) was calculated in terms of reflectance using Eq. (4) and the calculated linear refractive index of the BMST crystal is found to be n = 2.41. The optical studies revealed that, BMST crystal possesses good optical behavior for using it in device applications.

Kurtz powder SHG test

The second harmonic generation property of the BMST crystal was examined by using Kurtz powder SHG test [45]. The fundamental beam obtained from 1064 nm Q-switched Nd:YAG laser radiation of 2.8 mJ/pulse with 10 Hz repetition rate was used. In the present study, the crystalline powder was sieved into different particle size ranges such as 100, 120, 140, 160 µm. The Urea samples were used as reference for the SHG test. The ground BMST and Urea samples were loaded into uniform bore glass capillaries, which is having an inner diameter of about 600 µm. The sample was subjected to 1064 nm monochromatic radiation and green signal (532 nm) was observed from the sample. It confirms the capacity of frequency conversion (SHG) property of the BMST material. The intensity of the green signal was detected using monochromator, PMT, and oscilloscope. The output SHG signal voltages of the different sized powdered samples were observed to be 32, 40, 44 and 47 mV for 100, 120, 140 and 160 µm respectively and the reference Urea showed 10 mV. It is observed that the SHG intensities increase with increase in particle size (Fig. 11). The relative SHG efficiency of BMST is about 4.7 times that of Urea at about 160 µm particle size and also it agrees with the reported data. The counter-anion and cation substituted DAST derivative crystals exhibited strong second-harmonic signals by powder SHG test. The powder SHG efficiencies of few counter-cation substituted stilbazolium derivative crystals such as MBST [46], HMSB [47] and CMST [48] are compared and given in Table 4.

Photoluminescence spectra

Luminescent materials are substances which convert incident energy input into the emission of electromagnetic waves in the ultraviolet, visible or infrared regions and above that due to black-body emission. Photoluminescence (PL), where the luminescence is stimulated by UV or visible light, is a widely used technique to identify the impurities and finds applications in lighting technologies [49]. It is the mechanism through which the excited specimen relaxes to the equilibrium state. Luminescence processes



Fig. 11. Kurtz powder SHG signal voltage vs. particle size (µm).

Table 4

Comparison of powder SHG efficiency of BMST with some DAST based organic crystals.

Crystal	SHG efficiency	References
DAST	1000	[14]
MBST	17	[46]
HMSB	11	[47]
CMST	10.2	[48]
BMST	4.7	Present work

is being excited using a beam of light that leads to the creation of an electron-hole (e-h) pair and it may recombine across the gap and emit a photon with energy equal to band gap [50]. The e-h recombination process can be occurred because, excited electron and hole cannot remain in their initial excited states for very long, instead they can relax very rapidly (\sim 10–13 ns) to the lowest energy states within their respective bands by emitting phonons. Fig. 12 shows the room temperature PL spectrum of BMST crystal, which is excited at 360 nm. The donor-acceptor type and ionic property of the compound may give rise to luminescence. The broad photoluminescence emission (PLE) peak seen in the spectra at 432 nm is due to interaction between the electronic system of the luminescent center and the vibrations of ions which have it. Such a broad PLE emission was caused by diverse electronic transitions occurring in different energy levels due to deep or shallow holes within the band gap [51]. PL spectra consists two main peaks and one is near band edge transition usually lying at the ultraviolet region at 432 nm and other is in red region at 646 nm, which is related to deep level defect transitions. The tail band structure PL emission peak at 646 nm is due to the defects of the crystal [52]. The deep holes are origin states for the green, yellow, orange and red PL emissions, while the shallow holes are responsible for the violet and blue emissions [53]. In the present study, broad PL emission at 432 nm violet emission is an indicative of the charge transfer process as well as the trapping of electrons and it is due to the contribution of the shallow holes than the deep holes [54]. In addition, the weak PL emission peak at 646 nm is due to fewer contributions from deep holes in the energy levels. Thus, PLE spectrum revealed that, BMST crystal exhibits blue shift emission, which is most useful for luminescent applications.

Laser induced damage threshold study

Laser-induced damage (LID) in optical materials refers to permanent damage caused by melting, ablation, cracking, plasma



Fig. 12. Photoluminescence emission spectrum of BMST crystal excited at 360 nm.

formation, etc., when an optical material exposed to laser radiation. LID threshold refers to the fluence, which causes such damages. LID threshold of the optical materials are getting an important role due to high optical intensities involved in nonlinear process and it must withstand to high power intensities [55]. For LID experiment, the Q-switched 1064 nm Nd:YAG pulsed laser was used. The laser beam profile with repetition rate of 10 Hz and pulse width of 6 ns was used. The (100) plane of the crystal was polished and subjected to the LID threshold measurement. The polishing technique of the material produces minimum subsurface damage and it can be raised the surface damage threshold. The rear surface damages occurred due to Fresnel reflection loss at the front surface result in less energy [56]. The multishot LID measurement was made on the crystal with 1 mm beam spot. The output intensity of the laser was controlled with variable attenuator and delivered on the surface of the sample located at the near focusing of the converging lens. The energy density (E) of the laser beam was noted for which the crystal gets damaged. The surface LID threshold of BMST crystal was calculated using,

$$P(d) = E/\tau A \tag{5}$$

where *E* is the intensity of the irradiant laser beam (mJ), τ is the pulse width (ns) and *A* is the area of the circular spot size (cm²). The calculated LID threshold value of BMST crystal is found to be 1.50 GW/cm². Further, the LID threshold values are compared with familiar NLO crystals and are given in Table 5 [57,58]. It is clear that, BMST possesses lesser LID than DAST crystal and has higher value than KDP crystal, which is most widely used in NLO applications.

Thermal analyses

Thermogravimetric analysis measures the change in mass of a sample on heating and useful to study the crystallization. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are quite useful, since they provide reliable information on the physico-chemical parameters, characterizing the processes of transformation of solids or participation of solids in processes of isothermal or non-isothermal heating [59,60]. The SDT Q600 V8 instrument was used to record TG-DTA thermogram of the compound in nitrogen atmosphere at the heating rate of 20 °C/min (Fig. 13). The TGA curve revealed that, three distinct weight losses stages occurred on sample: the first one at about 294.93 °C connected with ~2% mass loss was accompanied by endothermic effect and was attributed to the removal of moisture absorbed by the compound. The second one begun at about 294.93 °C after melting and it extended up to 474.5 °C. It is connected with \sim 71% mass loss which is indicative for the decomposition of pyridine moiety, vaporization and burning of volatile gaseous such as SO₂, CO₂, and NO₂ produced from the thermal degradation of the compound. Similarly in the DTA- curve, one main endothermic peak was observed at about 288.07 °C and it is connected with melting of the compound. After the melting temperature, compound led to decomposition on further heating. The third decomposition step at temperature above 474.5 °C was observed in

 Table 5

 Comparison of laser damage threshold value of BMST crystal with some well-known NLO crystals.

Crystal	Laser damage threshold (GW/cm ²)	References
KDP	0.2	[57]
Urea	1.5	[57]
Beta-barium borate	5.0	[57]
L-Arginine phosphate	10.0	[57]
DAST	2.8	[58]
BMST	1.24	Present work



Fig. 13. TG-DTA thermogram of BMST compound in N₂ atmosphere.



Fig. 14. DSC curve of BMST crystal.

the course of TG-curve, which is extended up to 731.07 °C. It may be due to the change of the structure of the material and it is connected with ~26.8% mass loss which is indicative of break of vinyl ligand (C=C). The DSC analysis was carried out (Fig. 14) for the sample using EXSTAR SII DSC 6220 instrument. A sharp endothermic peak observed at about 289.4 °C is due to endothermic absorption of about 180 mJ/mg energy. It indicates that the sharp melting point nature of the crystal and also the indication of absence of impurities. TG-DTA and DSC analyses confirm that, BMST crystal melts at about 289.4 °C and then it starts to degradation. Thus, it is capable to function at temperature up to 289.4 °C in optical applications.

Conclusion

A novel DAST derivative crystal, 4-bromobenzaldehyde-4'-N'methylstilbazolium tosylate salt was synthesized by condensation method and the elemental analysis confirmed its composition. The solubility and metastable zone width of the synthesized salt in methanol solvent was determined and single crystals of BMST with dimension of $9 \times 3 \times 3$ mm³ were grown by solvent evaporation method. IR and Raman frequencies explored all the functional groups present in the compound. All the chemical shifts of functional groups of compound were confirmed by using ¹H NMR spectral studies. The single crystal X-ray diffraction study reveals that BMST crystallizes in the space group of $P2_1/c$ with monoclinic system. The equilibrium morphology of grown crystal was determined using WinXMorph program. The crystal perfection was studied by using HRXRD analysis. The optical transmission spectrum confirms that, crystal possess transmission window in 419–900 nm region and band gap energy (E_g) and linear refractive index were found to be 2.96 eV and 2.41 respectively. The SHG property was analyzed for different particle sizes by Kurtz method and found that SHG intensity increases with increase in particle size. Photoluminescence spectral studies suggest that strong charge transfer occurs in the molecule. Laser damage threshold study confirms that, BMST possess greater LID threshold than familiar NLO crystals such as KDP crystal. The decomposition stages were analyzed from thermal analyzes and found that the melting point is 289.4 °C; hence, it suggests the application limit. From the characterization results, it is observed that the BMST crystal is potential material for optical applications.

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