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### Bulk size crystal growth, spectroscopic, dielectric and surface studies of 4-N, Ndimethylamino-4-N'-methylstilbazolium m-nitrobenzenesulfonate (DSMNS): A potential THz crystal of stilbazolium family

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### Abstract

The synthesis and growth of a potentially useful and efficient nonlinear optical organic 4-N. N-dimethylamino-4-N'-methylstilbazolium single crystal of mnitrobenzenesulfonate (DSMNS) is reported. The growth experiment involved the slope nucleation method coupled with slow cooling as well as slow solvent evaporation techniques. Single crystal X-ray diffraction (XRD), Fourier transform infrared (FT-IR), FT-Raman and nuclear magnetic resonance (NMR) techniques have been employed to ascertain the structure and composition of the crystal. Second harmonic generation (SHG) efficiency of the sample has been examined by Kurtz and Perry powder test. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques are employed to investigate the thermal behavior of the grown crystal. The frequency/temperature dependent dielectric properties of the organic crystal of DSMNS are studied. The surface features of the grown crystal are investigated by chemical etching study and atomic force microscopy (AFM).

**Keywords:** Stilbazolium derivatives; Nonlinear optical material; Growth from solutions; Spectral analysis; Thermal analysis

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### 1. Introduction

The design and synthesis of organic materials for high second order nonlinear optical (NLO) effect has become a hot area of research due to their widespread applications in the fields of optical signal processing, integrated photonics, optical switching, optical data storage, electro-optic modulation, spectroscopy and, terahertz (THz) wave generation and detection [1-4]. THz wave, being a non-ionizing source, its generation and detection assumes significance in the field of nonlinear spectroscopy and biomedical imaging [5, 6]. Organic materials exhibiting large macroscopic nonlinearity can be potentially used for the generation of high power THz wave [7]. Hence, researchers are aiming at the development of organic materials particularly; ionic organic crystals with high chromophore density are of special interest for large NLO effect. The stable packing of chromophores in this class of crystals results in high thermal, mechanical and photochemical stability [8]. Among the various ionic organic crystals, 4-N, N-dimethylamino-4-N'-methylstilbazolium tosylate (DAST) is one of the widely reported crystals [9]. The generation of THz wave employing DAST crystal has been investigated recently using optical rectification (OR) and difference frequency generation (DFG) methods [10, 11]. DAST crystal consists of a stilbazolium cation and tosylate anion with strong columbic interaction, overwhelming the dipole-dipole interaction and thereby facilitating the formation of polar sheets of cation [4]. It is evident from the literature that the stilbazolium cations are the most attractive species and their molecular nonlinearity can be easily preserved by the introduction of novel counter-ions. The counter anion approach has boosted the research to explore diverse design possibilities by effectively varying the structure with a suitable anion to achieve the desired physical and chemical properties [12]. Every minor change in the structure of counter anion is found to have an important effect in the crystal stacking. Moreover, well designed counter anions have resulted in noncentrosymmetric structure with higher second order NLO activity close to or better than DAST [1, 13-15]. In the recent past, our research group has been involved in the growth of a few stilbazolium derivatives such as 4-N, N-dimethylamino-4-N'-methylstilbazolium 4styrenesulphonate (DSSS), 4-N, N-dimethylamino-4-N'-methylstilbazolium pmethoxybenzenesulfonate (DSMOS) and 4-N, N-dimethylamino-N'-methylstilbazolium pchlorobenzenesulfonate (DASC) [16-18]. In our continued efforts to develop ionic organic crystal with potential THz properties, in this article we are reporting on 4-N, Ndimethylamino-4-N'-methylstilbazolium m-nitrobenzenesulfonate (DSMNS), yet another stilbazolium derivative with promising physicochemical properties. The title compound (DSMNS) was synthesized by changing the tosylate anion of DAST with m-

nitrobenzenesulfonate, without altering the stilbazolium cation. In an early attempt, Okawa et al. have synthesized DSMNS along with various other derivatives. The crystal of DSMNS in its powder form had shown second harmonic generation (SHG) activity [19]. However, the grown samples of DSMNS were thin needle crystal of mm size only. In the present work, our effort has been directed to explore the possibilities to grow good quality macro size crystals of DSMNS in order to realize its practical applications for THz generation and electro-optic (EO) modulation. We have made an attempt to grow the DSMNS crystal via slope nucleation method coupled with slow cooling (SNM-SC), an efficient technique employed by our research group and also a few other researchers for developing DAST and its derivatives [16, 20]. The crystal was also grown by the slope nucleation method coupled slow solvent evaporation (SNM-SE) technique and the results are compared. Further, attention has been paid to investigate the structural, spectral and physicochemical properties of the grown crystals. Detailed investigations including Fourier transform infrared (FT-IR), FT-Raman, nuclear magnetic resonance (NMR) spectroscopic studies, dielectric measurement and surface properties of the crystal are reported for the first time.

### 2. Experimental Procedure

#### 2.1. Material synthesis

The chemicals employed in this work were of analytical grade (Sigma Aldrich) with high purity. DSMNS was synthesized by metathesization of 4-N, N-dimethylamino-4-N'methylstilbazolium iodide (DMSI) with silver m-nitrobenzenesulfonate. In the first stage, DMSI was synthesized by Knoevenagel condensation [21], where carbon-carbon  $\pi$ -bond between dimethylamino benzaldehyde and active hydrogen compound of 1, 4 dimethyl pyridinium iodide is formed by eliminating the water molecule from it in the presence of piperidine. In our experiment, 1, 4-dimethyl pyridinium iodide (2.35 g, 10 mmol) and 4-N, Ndimethylaminobenzaldehyde (1.79 g, 10 mmol) were dissolved in 30 ml of methanol in the presence of piperidine and condensed to form DMSI under mild conditions. The above mixture was refluxed for several hours at 70 °C using the Dean-Stark apparatus. The product was then cooled to room temperature and the red colored crystalline salt was obtained. The product was initially recrystallized in methanol and then in ethanol for at least 3-4 times to eliminate the unreacted materials. During the second stage, silver m-nitrobenzenesulfonate was synthesized by separately dissolving equimolar ratio of sodium m-nitrobenzenesulfonate and silver nitrate in minimum quantity of water. The prepared solutions were thoroughly mixed and stirred for several minutes to obtain a turbid white precipitate and the product was

dissolved by gentle heating. The resultant solution was filtered and the filtrate was heated to achieve the required supersaturation and then cooled naturally. Thus obtained precipitate of silver m-nitrobenzenesulfonate was collected by filtration.

The title compound (DSMNS) was synthesized by metathesization reaction, adopting the procedure previously reported [19]. The reaction scheme is illustrated in Fig.1. Initially, DMSI cation (0.732 g, 2 mmol) was dissolved in 50 ml of methanol under mild heat. Simultaneously, in another beaker, silver m-nitrobenzenesulfonate (0.62 g, 2 mmol) was dissolved in 30 ml of methanol under moderate hot conditions. Thereafter the two hot solutions were thoroughly mixed through magnetic agitation which forms a precipitate immediately. The content was stirred for about 30 minutes and then the silver iodide byproduct was removed by filtration. The filtrate was then concentrated to supersaturation upon heating and then cooled to ambient temperature. The resulting DSMNS precipitate was collected by suction filtration. The purity of the synthesized DSMNS powder was further improved by recrystallization in methanol for at least 5-6 times.

### 2.2. Solubility

The solubility of the as-synthesized DSMNS salt in methanol solvent was estimated at different temperatures (35, 45, 55 and 65 °C). It is evident from the solubility diagram (Fig.2) that DSMNS has a positive solubility coefficient in methanol, thus encouraging its growth by low temperature solution growth methods. Interestingly, quite a few stilbazolium crystals were reported to grow favorably in methanol solvent while grown by slow solvent evaporation or slow cooling techniques [13, 17].

### 2.3. Crystal growth

Crystal growth of DSMNS was achieved by employing slope nucleation method coupled with slow cooling (SNM-SC) technique and also via slope nucleation method coupled with slow evaporation (SNM-SE) technique. For achieving growth by SNM-SC, the saturated solution was prepared by dissolving 2.0 g of DSMNS in 100 ml of methanol at 55 °C. The saturated solution was filtered and then shifted to a Teflon beaker. To promote slope nucleation, a Teflon plate with parallel grooves was kept inside the beaker. The beaker was then sealed with a cap and kept in a constant temperature bath at 50 °C and then slow cooled at a rate of 0.5-1 °C/day. After 20-25 days, crystals with size up to  $14 \times 1 \times 1 \text{ mm}^3$  were harvested. The crystals appeared reddish (Fig. 3a) with predominantly needle shape, possessing a fairly flat surface. In order to grow the crystal by SNM-SE technique, the saturated solution was prepared by dissolving the synthesized powder in 200 ml of methanol

at 35 °C. The prepared solution was kept in a Teflon beaker and then sealed with a perforated lid and housed in a constant temperature bath to encourage the slow solvent evaporation. After 3-4 weeks, bulk size crystals of size up to 2.5 cm in length, 3 mm in breadth and 2 mm in thickness were harvested. The bulk size crystals grown from SNM-SE technique are shown in Fig. 3b. It is evident that the DSMNS crystals grown by slow evaporation technique tend to grow much thicker and broader than those grown by SNM-SC, but their surface is rather rough and the edges are not sharp. The crystals grown in the present work are at least 7 fold bigger than the previously reported size [19]. The improvement in size is attributed to the slope nucleation method which enables efficient control of nucleation and growth habit.

#### 2.4. Characterization

Single crystal X-ray diffraction data were collected by using a Bruker X8 KAPPA APEX II single crystal X-ray diffractometer with MoK<sub> $\alpha$ </sub> ( $\lambda = 0.71073$  Å) radiation. The FT-IR spectrum of DSMNS was recorded in the region 400-4000 cm<sup>-1</sup> with a Perkin-Elmer FT-IR spectrometer using KBr pellet technique. The NIR FT-Raman spectrum of DSMNS was recorded with a Bruker RFS 27: stand alone FT-Raman spectrometer using a Nd:YAG laser at 1064 nm with a 470 mW output as the excitation source. The proton NMR spectrum was recorded employing a Bruker ADVANCE III 500 MHz FT-NMR spectrometer by dissolving the sample in deuterated methanol. The NLO test was done on the sample using a Q-switched mode locked Nd:YAG laser (1064 nm, Quanta ray series, Spectra Physics) with a beam of energy 10 ns pulse width and 0.68 J power. The TG/DTA thermal analyses for DSMNS powder sample were carried out between 25 and 500 °C using a Perkin Elmer TGA-7 thermal analyzer at a heating rate of 10 °C per minute. The DSC thermogram of DSMNS was obtained using a Perkin Elmer DSC-7 differential scanning calorimeter. For dielectric measurements HIOKI 3532-50 LCR Hitester was employed. A sample of known dimension was silver coated and then placed inside a dielectric cell. The capacitance was measured at different temperatures (308, 328, 348 and 368 K) and frequencies (50 Hz to 5 MHz). The chemical etching analysis was carried out using a Nikon Eclipse LV100 POL microscope. The surface features of the DSMNS crystals were analyzed by atomic force microscopy (AFM) employing the Park systems XE-70 (South Korea). All measurements were performed at room temperature, and images were collected in non-contact mode at a scan rate of 0.5 Hz. In this mode, the tip hovers around 50-150 Å above the sample surface. Attractive van der Waals forces acting between the tip and the sample are detected, and topography images are constructed by scanning the tip above the surface.

### 3. Results and Discussion

### 3.1. Single crystal XRD analysis

Single crystal XRD data of the DSMNS crystal is presented in Table. 1. It is observed that the grown crystal belongs to *monoclinic* system with space group  $P2_1$ . The results obtained in the present work are in concurrence with the literature and thus confirms the identity of DSMNS [19].

#### 3.2. FT-IR and FT-Raman spectral analyses

The infrared and Raman spectroscopy are essential tools to identify various kinds of vibrational modes present in the molecules [22]. Vibrational frequencies depend on the bonds, crystal structure and field force experienced by the atoms and hence vital information on intermolecular interactions of the molecules can be obtained [23]. The vibrational spectral analysis of DSMNS sample was performed on the basis of the characteristic vibrations of the stilbazolium cation and nitrobenzenesulfonate anion. The overall stilbazolium cation vibrations comprise of the vinyl group, phenyl and pyridine rings, methyl and skeletal mode. The anion (m-nitrobenzenesulfonate) consists of aromatic nitro and sulfonate group vibrations. The FT-IR and FT-Raman spectra recorded for the DSMNS crystal are depicted in Fig. 4 and 5, respectively.

#### 3.2.1. Vinyl group vibrations

The vibrations of ethylenic bridge are very sensitive to the degree of charge transfer between the donor and the acceptor groups, hence such stretching modes draw the special attention of the spectroscopists. The alkene bond stretching vibrations in conjugated systems without a center of symmetry are likely to produce two C=C stretching bands, one near at 1650 cm<sup>-1</sup> and the other one at 1600 cm<sup>-1</sup> [23]. The bands observed at 1647 and 1589 cm<sup>-1</sup> in the IR and those at 1618 and 1586 cm<sup>-1</sup> in the Raman spectra can be attributed to the C=C stretching vibrations of ethylenic bridge. [24]. The aliphatic C–H stretching bands for stilbazolium derivatives are expected in the region between 3050 and 3000 cm<sup>-1</sup> [23, 25]. In DSMNS crystal, the weak band observed at 3074 cm<sup>-1</sup> (IR spectrum) can be attributed to the aliphatic C–H stretching.

### 3.2.2. Phenyl and pyridine ring vibrations

The aromatic ring vibrational modes of DSMNS have been analyzed on the basis of stilbazolium ring vibrations that are composed of para disubstituted phenyl and pyridine rings connected by ethylenic bridge. The C–H in-plane and out-plane bending vibrations are observed in the regions 1300-1000 cm<sup>-1</sup> and 1000-675 cm<sup>-1</sup>, respectively [23]. The C–H in-

plane bending vibrations are marked as characteristic bands at 1215, 1180, 1164 and, 1033 cm<sup>-1</sup> in the IR spectrum and at 1206, 1183 and 1617 cm<sup>-1</sup> in the Raman spectrum. The C–H out-of-plane bending vibrations are observed in the IR spectrum at 970, 945, 875 and 756 cm<sup>-1</sup>, where as it is observed in the Raman spectrum at around 776 cm<sup>-1</sup>. The 1, 4 distributed aromatic ring C–H vibration is expected in the region of 800-875 cm<sup>-1</sup> [26]. The peak at 825 cm<sup>-1</sup> in the IR spectrum is attributed to the 1, 4 distributed aromatic ring C–H. The phenyl ring mode deformation vibrations are observed at 663, 613 and 532 cm<sup>-1</sup> in the IR spectrum, and at 722, 666, 615 and 532 cm<sup>-1</sup> in the Raman spectrum [23].

### 3.2.3. Methyl group vibrations

Methyl groups are normally referred to as an electron donating substituents in the aromatic ring system [23]. For methyl (CH<sub>3</sub>) group, the asymmetric stretching vibrations manifest as characteristic bands at 2916 and 2956 cm<sup>-1</sup> in the IR and Raman spectra, respectively. The asymmetrical and symmetrical bending vibrations of CH<sub>3</sub> group are expected in the regions of 1465-1440 and 1390-1370 cm<sup>-1</sup>, respectively [27]. The band positioned at 1473 cm<sup>-1</sup> in the IR and the other band at 1474 cm<sup>-1</sup> in Raman spectra have been assigned to the asymmetrical bending vibrations of methyl group. The intense IR band observed at 1369 cm<sup>-1</sup> can be attributed to the symmetrical bending vibrations. For CH<sub>3</sub> group, the rocking mode usually appears in the region 1070-1010 cm<sup>-1</sup> [23]. This mode appears as the weak band at 1072 cm<sup>-1</sup> and 1047 cm<sup>-1</sup> in the IR and Raman spectra, respectively.

### 3.2.4 Sulfonate group vibrations

The SO<sub>2</sub> group gives rise to asymmetric and symmetric stretching vibrations in the range 1420-1000 cm<sup>-1</sup> with high intensity peaks. At the same time, the wave numbers of the SO<sub>2</sub> compounds may overlap with those of other functional groups [28]. In DSMNS crystal, the strong bands at 1180 and 1164 cm<sup>-1</sup> in the IR, and those at 1183 and 1167 cm<sup>-1</sup> in the Raman spectra are characteristic of SO<sub>2</sub> asymmetric stretching vibrations. Thus the bands observed at 1072 cm<sup>-1</sup> in the IR spectrum and at 1047 cm<sup>-1</sup> in the Raman spectrum can be assigned to the SO<sub>2</sub> symmetric stretching vibrations. The band seen at 494 cm<sup>-1</sup> in the IR spectrum and the band at 500 cm<sup>-1</sup> in the Raman spectrum can be attributed to SO<sub>3</sub> deformation [23].

### 3.2.5. Nitro group vibrations

For an aromatic nitro compound, the strong absorption bands due to the asymmetric and symmetric vibrations of the NO<sub>2</sub> group are expected in the region 1560-1500 cm<sup>-1</sup> and 1360-1300 cm<sup>-1</sup>, respectively [28]. The very strong IR band viewed at 1523 cm<sup>-1</sup> and the

Raman band at 1514 cm<sup>-1</sup> can be attributed to the NO<sub>2</sub> asymmetric stretching vibrations. The strong bands seen at 1346 cm<sup>-1</sup> in the IR and at 1338 cm<sup>-1</sup> in the Raman spectra are assigned to the NO<sub>2</sub> symmetric stretching vibrations.

### 3.2.6. Skeletal mode vibrations

The absorption bands for C–N and C–C stretching vibrations are generally identified in the region 1150-850 cm<sup>-1</sup> [23]. The bands positioned at 876 cm<sup>-1</sup> and at 875 cm<sup>-1</sup> in the IR and Raman spectra are assigned to C–N stretching mode.

### 3.2.7. Other vibrations

The band noticed at wavenumber 3448 cm<sup>-1</sup> corresponds to the O–H stretching, which might be due to the air moisture. The Raman band observed at 85 cm<sup>-1</sup> is possibly attributed to the CH<sub>3</sub> torsional vibration [23]. The FT-IR and FT-Raman wavenumbers (cm<sup>-1</sup>) and their assignments for DSMNS crystal are presented in Table 2.

### 3.3. NMR analysis

The proton NMR spectrum (Fig. 6) of DSMNS was recorded by dissolving the sample in deuterated methanol. The singlets at 3.08 and 4.23 ppm are assigned to the six hydrogens of N–(CH<sub>3</sub>)<sub>2</sub> and three hydrogens of N–CH<sub>3</sub>, respectively. The intensity of the peak at 3.08 ppm substantiates the number of contributing nuclei. The doublets positioned at 6.79 and 7.62 ppm are due to the four hydrogens of (CH<sub>3</sub>)<sub>2</sub>–N–C<sub>6</sub>H<sub>4</sub> aromatic ring. The doublets at 7.79 and 8.52 ppm represent the four hydrogens of C<sub>5</sub>H<sub>4</sub>N aromatic ring. The doublets seen at 7.11 and 7.85 ppm are due to the two oliphinic hydrogen atoms (HC=CH). The doublets observed at 8.20 and 8.63 ppm are corresponding to the two aromatic hydrogens that are present in the positions ortho to –SO<sub>3</sub>. The doublet seen at 8.32 ppm is assigned to the aromatic hydrogen ortho to nitro group alone. The triplet observed at 7.72 ppm is due to the aromatic hydrogen which present in the meta position to both NO<sub>2</sub> and SO<sub>3</sub> groups.

### 3.4. CHN analysis

The calculated CHN values of  $C_{22}H_{23}N_3O_5S$  are; C = 59.85%, H = 5.25% and N = 9.52% and the corresponding experimentally found values are; C = 59.81%, H = 5.24% and N = 9.39%. Both the theoretical and experimental values resemble each other.

### 3.5. SHG efficiency test

The second harmonic generation (SHG) efficiency of DSMNS was performed by Kurtz and Perry technique [29]. The sample was made into a very fine powder and tightly packed in a microcapillary tube. It was then mounted on the path of a Q-switched Nd:YAG laser (1064 nm, Quanta ray series) of pulse width of 10 ns with 0.68 J power. The SHG signal

generated at 532 nm is split from the fundamental frequency using an IR separator. Microcrystalline powder sample of urea was employed as the reference material to compare the efficiency of the DSMNS. When a laser beam of 0.68 J was passed through the sample, an output pulse of 382 mV was recorded for DSMNS. The SHG study confirmed that DSMNS crystal exhibits an efficiency which is nearly 27 times higher than that of the urea crystal.

#### 3.6. Thermal analysis

From the TG curve (Fig. 7a), one can ascertain that the sample is thermally stable up to 237 °C and it decomposes immediately after melting. The material undergoes a weight loss of 53.56% from 237 °C up to 486.5 °C and the remaining 46.4% of the sample is left out as residue at 500 °C. The endothermic peak at 235.1 °C in the DTA curve (Fig. 7a) could be attributed to the melting of the material. Another exothermic peak positioned at 323.2 °C, could be assigned to the complete breakage of stilbazolium ion. The DSC thermogram (Fig. 7b) shows an endothermic peak at 235.4 °C with a thermal heat capacity of 96 J/g, representing the melting point of the material. The observed melting point of DSMNS is slightly lower than the DAST (259 °C) [20]. However, organic materials with thermal stability above 200 °C could be considered as thermally stable materials for realizing practical applications.

#### 3.7. Dielectric studies

Fig. 8a illustrates the variation of dielectric constant ( $\varepsilon_r$ ) of DSMNS crystal as a function of log frequency at different temperatures. It is noticed that at a constant temperature, the dielectric constant decreases with frequency. The high dielectric constant at low frequency is due to the existence of electronic, ionic, dipole orientation and space charge polarizations [30]. At low frequencies, all the four contributions may be active. Particularly, the higher value of dielectric constant at low frequency is due to the space charge polarizations that depend on the purity and perfection of crystals [31, 32]. When the frequency increases, the net polarizations of the material drops to zero since, the entire polarizations end to contribute and it appears in the graph as an exponential reduction in the dielectric constant value. The variation of dielectric loss (tan  $\delta$ ) with frequency (Fig. 8b) is also measured. Fig. 8b shows that the dielectric loss decreases with increasing frequency [33]. At low frequencies, the dielectric loss is high and it can be related to the space charge polarizations owing to the charged lattice defect [34]. The low dielectric constant of the materials at high frequency is an added advantage for photonics and electro-optic device

fabrications [35]. It has been already reported that DAST, a prominent crystal of stilbazolium family has low dielectric permittivity with much higher electro optic (EO) coefficient [3]. Based on the dielectric study, it can be concluded that DSMNS, a derivative of stilbazolium possesses low dielectric constant at high frequencies and hence the material is potentially suitable for EO applications.

### **3.8.** *Etching studies*

Chemical etching study is very simple and suitable technique to reveal the crystal defects and growth mechanism by knowing the microstructural imperfection or dislocation of the grown crystal [36]. Etching study was made on the DSMNS crystal grown by both SNM-SC and SNM-SE techniques. Methanol was utilized as an etchant and the experiment was performed at room temperature. The crystals were immersed in the etchant for an etching time of 10 and 15 s and then gently wiped with tissue paper. The etched patterns were then examined under an optical microscope. Fig. 9 (a) and (b) displays the etch patterns recorded on the surface of DSMNS crystal grown by SNM-SC. It is observed from Fig. 9a that striation like etch pit patterns are formed with an etching time of 10 s, while increasing the etching time to 15 s, a clearly visible and deep etch pit pattern is spotted at the dislocation site (Fig. 9b). Moreover, the further increase in etch time has not produced any change in the morphology of etch pit and the observed pattern was stable over a longer period. Fig. 10a and b demonstrates the etch patterns of DSMNS crystal grown by SNM-SE technique. This etch pit pattern is more or less similar to those crystals grown by SNM-SC, but the density of striation-like pattern is found to be more and also irregular in shape. Compared to SNM-SE grown crystal, the number of etch pits is relatively less in SNM-SC grown crystal and this could be attributed to the difference in growth condition which influences the crystalline perfection.

### 3.9. Atomic force microscopy

AFM provides a three dimensional (3D) profile of the surface on a nanoscale, it measures the forces between a sharp probe (<10 nm) and the surface at very short distance (0.2-10 nm probe-sample separation). To better comprehend the morphology of a surface, a quantitative description of the surface topography must be carried out. The topography matrix data should be treated in each profile line (2D) or over all profiles extending the analysis to surface (3D). Figs. 11&12 demonstrate the 2D and 3D image morphologies of the DSMNS crystals grown by SNM-SC and SNM-SE techniques, respectively. It is evident from the morphology (Fig. 11b) that the surface of the crystal grown by SNM-SC contains very few

major hillocks. Whereas, the crystal grown by SNM-SE (Fig. 12b) is free from major hillocks, but contains a deep cavity. It is well known that a large number of peaks and valleys in an image may significantly affect the average roughness ( $S_a$ ) and root mean square ( $S_q$ ) values [37]. The estimated roughness values for crystal grown by SNM-SC are found to be  $S_a$  = 15.775 nm and  $S_q$  = 18.930 nm. While, the values are quite higher ( $S_a$  = 23.337 nm and  $S_q$  = 30.038 nm) for the crystal grown by SNM-SE.

The ten point height  $(S_z)$  which is regarded as the difference in height between the average of the five highest peaks and the five lowest valleys along the assessment length of the profile.  $S_z$  is found to be 101.745 and 220.435 nm for DSMNS crystal grown by SNM-SC and SNM-SE, respectively. The Surface skewness  $(S_{sk})$  and kurtosis  $(S_{ku})$  moments are the parameters used to measure the asymmetry and flatness, respectively. It has been reported that if the height distribution is asymmetrical and the surface has more peaks than valleys, then the skewness moment is positive. If the surface is more planar and the valleys are predominant, the skewness is negative [37]. The  $S_{sk}$  values for the crystals grown by SNM-SC (0.409) and SNM-SE (0.558) are positive. Similarly, another important surface parameter, namely, Surface kurtosis  $(S_{ku})$  is the measure of surface sharpness. If the value of  $S_{ku}$  is lesser than 3, the surface is regarded as a perfectly flat one and if  $S_{ku}$  is greater than 3, the surface is set to have more peaks than valleys [38]. The  $S_{ku}$  values are found to be 2.564 and 4.038 for the samples grown by SNM-SC and SNM-SE, respectively. The  $S_{ku}$  values indicate that the DSMNS crystal grown by SNM-SC has moderately flat surface and free from cavities than the crystal surface of SNM-SE. The various roughness parameters of the as-grown crystal surfaces of DSMNS are listed in Table 3.

### 4. Conclusion

The bulk size crystals of DSMNS were successfully grown via SNM-SC and also from SNM-SE method using methanol solvent. Crystals grown by SNM-SC were found to have smooth surface with needle morphology. Though the SNM-SE method offers promise for achieving bulk size crystal growth, the harvested crystals require further improvement in terms of their surface features and morphology. Single crystal X-ray diffraction revealed the monoclinic crystal structure with space group  $P2_1$ . The crystal structure, molecular weight and the presence all the functional groups were confirmed by FT-IR, FT-Raman, CHN and NMR studies. The SHG efficiency of DSMNS was found to 27 times higher than the urea crystal. The TG/DTA and DSC thermograms confirmed that the DSMNS is thermally stable up to 235 °C. The material showed low dielectric constant at high frequency. The chemical etching and atomic force microscopic studies confirmed the moderately good surfaces of the

grown crystals. Thus the ability to grow as bulk size crystal of good crystalline quality coupled with high SHG activity and low dielectric constant of DSMNS crystal make it a potential candidate material for nonlinear optics, photonics and THz applications.

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### **Figure Caption**

- Fig.1. Synthesis scheme for DSMNS
- Fig. 2. Solubility curve for DSMNS in methanol
- Fig. 3. Photographs of DSMNS crystals grown by (a) SNM-SC and (b) SNM-SE techniques
- Fig. 4. FT-IR spectrum of DSMNS crystal
- Fig. 5. FT-Raman spectrum of DSMNS crystal
- Fig. 6. NMR spectrum of DSMNS crystal
- Fig. 7. (a) TG/DTA and (b) DSC thermograms for DSMNS crystal
- Fig.8. Frequency dependence of a) dielectric constant and b) dielectric loss of DSMNS
- **Fig.9.** Etch pattern observed for DSMNS crystal grown by SNM-SC for (a) 10 s and (b) 15 s
- **Fig.10.** Etch pattern observed for DSMNS crystal grown by SNM-SE for (a) 10 s and (b) 15 s
- Fig. 11. a) 2D and b) 3D AFM images of DSMNS crystal grown by SNM-SC
- Fig. 12. a) 2D and b) 3D AFM images of DSMNS crystal grown by SNM-SE

### **Table Caption**

 Table 1 Single crystal XRD data of DSMNS crystal

- Table 2 FT-IR and FT-Raman wavenumbers and their assignments of DSMNS
- Table 3 Roughness parameters of as-grown crystals surface of DSMNS



4-N,N-dimethylamino-4-N'-methylstilbazolium m-nitrobenzenesulfonate (DSMNS)

Fig.1. Synthesis scheme for DSMNS





Fig.2. Solubility curve for DSMNS in methanol



Fig.3. Photographs of DSMNS crystals grown by (a) SNM-SC and (b) SNM-SE techniques



Fig.5. FT-Raman spectrum of DSMNS crystal





Fig.7. (a) TG/DTA and (b) DSC thermograms for DSMNS crystal



**Fig.8.** Frequency dependence of (a) dielectric constant and (b) dielectric loss of DSMNS



Fig.9. Etch pattern observed for DSMNS crystal grown by SNM-SC for (a) 10s and



Fig.10. Etch pattern observed for DSMNS crystal grown by SNM-SE for (a) 10s and

(b) 15s



Fig.11. a) 2D and b) 3D AFM images of DSMNS crystal grown by SNM-SC



Fig.12. a) 2D and b) 3D AFM images of DSMNS crystal grown by SNM-SE

Table 1 Single crystal XRD data of DSMNS crystal.

	Formula Formula weight Crystal system Space group a (Å) b (Å) c (Å) c (Å) α (deg) β (deg) γ (deg)	C <sub>22</sub> H <sub>23</sub> N <sub>3</sub> O <sub>5</sub> S 441.50 Monoclinic P2 <sub>1</sub> 9.356 (6) 6.462 (5) 17.957 (10) 90 101.38 90	CRIPS
Table 2 FT	-IR and FT-Raman wave	numbers and their assignme	ents of DSMNS

	3448 w	-	O–H stretching
	3074 w	-	Vinyl C–H stretching
	2916 w	2956 vw	CH <sub>3</sub> asymmetric stretching
	1647 m	1618s	v (C= C)/vinyl C–H rock
	1589 vs	1586vs	Ring v (C=C)
	-	1550 s	Ring v (C=C)
	1523 vs	1514 s	N–O asymmetric stretch
	1473 m	1474 vw	CH <sub>3</sub> asymmetric deformation
	1442 m	1435 w	Ring v (C=C)
	1369 s	-	CH <sub>3</sub> symmetric deformation
	1346 s	1338s	N–O Symmetric stretch
	1315 s	1317 s	Ring v (C=C)
	1215 vs	1206 s	Ring δ (C–H)
	1164, 1180 vs	1167, 1183 s	Ring $\delta$ (C–H /v <sub>a</sub> (SO <sub>2</sub> )
	1072 m	1047 w	CH <sub>3</sub> rocking/v <sub>s</sub> (SO <sub>2</sub> )
	1033 s	-	Ring δ (C–H)
	970 m	-	Ring $\delta$ (C–H)
	945 m	-	Ring δ (C–H)
	876 s	875 vw	Ring $\delta$ (C–H)/C-N stretching
	825 s	-	1,4-Distribution of aromatic ring C–H
	756 s	776 w	Ring δ(C–H)
	-	722	Ring δ(CCC)
	663 s	666 vw	Ring δ(CCC)
	613 s	615 vw	Ring δ(CCC)
	532 s	532 vw	Ring δ(CCC)
	494 w	500 vw	SO₃ <sup>–</sup> deform
	-	85 w	CH <sub>3</sub> torsion
_			

Abbreviations: v-stretching;  $\delta$ -deformation vibration, v<sub>a</sub>-asymmetric stretching; v<sub>s</sub>-symmetric stretching; vs-very strong; s-strong; m- medium; w-weak; vw-very weak

Roughness parameters	Crystal	grown	by	Crystal	grown	by
Roughness parameters	SNM-SC	1		SNM-SE		

Roughness average (S <sub>a</sub> )	15.775 nm	23.337 nm
Root mean square (S <sub>q</sub> )	18.930 nm	30.038 nm
Surface skewness (S <sub>sk</sub> )	0.5583	0.409
Surface kurtosis (S <sub>ku</sub> )	2.564	4.038
Peak-peak roughness $(S_y)$	101.745 nm	220.435 nm
Ten point height $(S_z)$	101.745 nm	220.435 nm
Table 3 Roughness param	eters of as grown crystal	surface of DSMNS

### **Graphical abstract**



### Highlights

- $\geq$ A potentially useful ionic organic NLO crystal of DSMNS is grown in bulk size.
- > The growth is achieved by modified slope nucleation approach.
- > A detailed FTIR and FT Raman spectral analyses is carried out.

Acception