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Growth and characterization of halogen substitution in counter benzenesulfonate of organic nonlinear optical crystal: DASB

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Abstract

The organic stilbazolium derivative crystal 4-dimethylamino-4′-stilbazolium p-bromobenzenesulfonate (DASB) was successfully grown by spontaneous nucleation method coupled slow evaporation (SNM-SE) for the first time. The corresponding powder XRD revealed the crystalline nature of the DASB material, and various functional groups were determined by FT-IR. The thermal stability and melting point were analyzed by TG/DTG and DSC measurement. The absorption coefficient, band gap energy, cut-off wavelength and extinction coefficient were obtained through UV–NIR spectral study. Photoluminescence result indicates DASB crystal exists purple emission at 405 nm and 467 nm because of the π–π∗ and defect transitions, respectively. The SHG efficiency of DASB crystal is about 3 times higher than KDP crystal. All the encouraging results indicate the DASB crystal is a promising candidate for the THz generation applications.

1. Introduction

Recently, the research of terahertz (THz) technology has become an extremely attractive field. There exist intensive research efforts in frequency conversion, electro-optic modulation, optical parametric oscillation [1–4], and THz generation and detection [5], etc. Comparing with inorganic materials, the organic stilbazolium salts have several advantages, such as large molecular nonlinearity or first-order hyperpolarizability (β), long-term stability and higher tendency to override the dipole–dipole interactions and thus form non-centrosymmetric macroscopic packing [6–9].

Among the organic NLO crystals for THz generation, the most interesting crystal is 4-N, N-dimethylamino-4′-stilbazoliumtosylate (DAST) [10, 11], which can be used for frequency conversion, generation and detection of THz and high-speed electro-optic modulation, due to its large NLO susceptibility, large electro-optic coefficient and the lower dielectric constant [12–14]. However, DAST has its own drawbacks, such as the lower hardness, the absorption feature at 1.1 THz, and deliquescence [15]. Therefore, the purpose is to optimize the growth process and develop new molecules to promote crystal growth. The nonlinear optical polarizability of stilbazolium salts can be greatly improved by modifying the substituents on the anions [16, 17]. Almost all the stilbazolium tosylate crystals, which consist of stilbazolium cation and tosylate anion connected [15]. It has been demonstrated that the change of stilbazolium cation will affect the crystal nonlinearity. Using this approach, different kinds of cation derivatives have been obtained, such as BMST, HBST, CMST, and so on [15, 18, 19].

In addition to modifying counter cation can change the generation of nonlinearity, changing tosylate anion is another effective approach to design stilbazolium salt crystal. By modified counter anions, these stilbazolium derivatives have shown large potential to increase the noncentrosymmetric and crystal growth quality, results faster and easier growth of bulk crystal growth. In this connection, DAST derivatives producing crystals with
isomorphous of halogen substitution are good model compounds for the analysis of this phenomenon \([20]\), such as DASC and DASB \([18]\).

We have reported on the growth of DAST over the last few years \([21, 22]\) and its derivative, such as 4-hydroxy benzaldehyde-N-methyl 4-stilbazolium tosylate (HBST) \([15]\) and 4-chlorobenzaldehyde-N-methyl 4-stilbazolium tosylate (CMST) \([20]\), in order develop efficient organic THz sources, the growth process of DASB crystal was optimized in this work to further improve the crystal quality and control its morphology. The DASB crystal was grown in methanol and acetonitrile mixed solvent by the spontaneous nucleation method coupled slow evaporation (SNM-SE). The functional groups vibration and thermodynamic properties of the crystal have been investigated by the FT-IR spectra and TG/DSC spectra, respectively. Moreover, some previously unknown properties are also reported, such as calculating a series of optical constants by UV–vis-NIR spectroscopy, SHG signal and photoluminescence properties.

2. Experimental

2.1. Synthesis

DASB was synthesized by the condensation reaction between 4-(dimethylamino)benzaldehyde and 1,4-dimethylpyridinium p-bromobenzene- sulfonate \([18]\) (figure 1). DASB was synthesized through a two-step synthesis route: (1) 4-picoline (9.79 ml, 0.1 mol), 4-bromobenzenesulfonyl chloride (25.5 g, 0.1 mol) and sodium methylate (5.4 g, 0.1 mol, used as catalyst), all of them were added to 150 ml of methanol and acetonitrile mixed solution in a round bottom flask and refluxed for 36 h at 45 °C. (2) 4-dimethylaminobenzaldehyde (14.9 g, 0.1 mol) was added. In addition, the solution color turned into red gradually when added few of piperidine as a catalyst and the temperature gone up to 70 °C. After 48 h, the solution color become dark red and DASB raw materials were deposited at the bottom of the flask. The product was purified from methanol by recrystallization for five times and dried under vacuum at 100 °C for 2 h.

2.2. Crystal growth

Solubility is an important parameter for the concentration of the require material, the growth rate and the growth method. The solubility curve of DASB was measured by dissolving purified DASBA crystal in 100 ml of methanol, acetonitrile and the mixed solvent of methanol- acetonitrile \((1: 1)\) at different temperature in figure 2, respectively. The DASB can be dissolved in both methanol and acetonitrile, moreover, DASB crystals have higher solubility in the mixed solution and the solubility of DASB increases with the increase of temperature. As a result, methanol- acetonitrile was selected as the best solvent for crystal growth. Based on this, the spontaneous nucleation method is adopted for growing DASB crystals.

According to the solubility curve, the DASB crystals were grown by spontaneous nucleation method-slow evaporation (SNM-SE), and the growth solution was prepared with 400 ml of methanol- acetonitrile \((V_{\text{methanol}}: V_{\text{acetonitrile}} = 1:1)\) by dissolving 4 g of DASB raw material at 60 °C with stirring about 3 h. The prepared solution was filtered and transferred into a 600 ml glass beaker, maintains at 45 °C for 24 h. During growth, the cooling rate is 0.5 °C per day. After 30 days, the good quality single crystal of DASB with dimensions \(3 \times 3 \times 1\) mm\(^3\) were grown in figure 3(a). The crystal quality is better than that reported by Matsukawa et al \([18]\), which can be seen from the figure 3(b).
3. Results and discussion

3.1. Powder x-ray diffraction analysis

In the process of synthesis, it is easy to get the orange hydrate DASB in the presence of water. When heated to 100 °C, the crystalline powder of DASB hydrate turns deep red with a duration of 1–2 h. It was confirmed that the crystalline powder obtained after heat treatment was DASB by powder x-ray diffraction analysis. The peak at 11.73° and 16.86° were previously observed on DASB, in which these peaks were assigned to the signal from the (110) and (021) crystal plane of DASB. Two shape peaks at diffraction angles of 18.94° and 19.84°, assigned to the respective signals from the (022) and (00-4) crystal planes of DASB. Moreover, there are also a few smaller peaks, which are 25.66°, 27.30° and 30.05°, corresponding to the (024), (-3-11) and (133) planes of the crystal, respectively. The experimental powder x-ray diffraction pattern of DASB is in good agreement with the literature data[23] as shown in figure 4. The datasheet of diffraction peaks for XRD result of the crystal was shown in table 1.

3.2. FT-IR spectral analysis

The sample was characterized by Fourier infrared spectroscopy (FT-IR) to determine their function groups and vibrational modes. The FT-IR spectrum was recorded in the region 400–4000 cm⁻¹ by using Nicolet 6700 Fourier transform infrared spectrometer and the spectrum of DASB compound is showed in figure 5. Due to the C=C stretching vibrations of vinyl bridge and the aromatic ring of the chromophore, the absorption peaks were formed at 1639.81 cm⁻¹ and 1583.20 cm⁻¹, respectively. Because of the aromatic C–H stretching vibration, a peak is formed at 3037.15 cm⁻¹. The peaks at 1517.80 cm⁻¹ and 1336.34 cm⁻¹ can be attributed to the vibrations of the aromatic ring and the symmetrical bending vibrations of methyl groups, respectively. Due to asymmetric stretching vibration character of SO₃ group, a peak occurred at 1162.75 cm⁻¹. The existence of

![Figure 2. Solubility curves of DASB.](image)

![Figure 3. Photograph of DASB crystal (a) grown by SNM-SE, (b) micrograph observed on the (001) face.](image)
conjugate π and the sulfonic group are related to the molecular polarization of DASB and lead to its strong nonlinear optical effect \([15]\). In the region 1070–1010 cm\(^{-1}\), which is due to the rocking of CH\(_3\) group \([24]\). The details of vibration peaks are shown in table 2.

### 3.3. Thermal analysis

To ascertain the thermodynamic properties of DASB powder, the TG-DTG and DSC measurements were performed using NETZSCH STA 449F5 analyzer equipment in a N\(_2\) atmosphere at a heating rate of 15 °C min\(^{-1}\). The TG-DTG thermogram of DASB powder is shown in figure 6(a). It indicates that the DASB crystal starts decomposing at around 300 °C. More over, there are three different weight losses stages on

![Figure 4. XRD patterns of DASB. The upper curve is the experimental XRD pattern of DASB and the bottom curve is the simulated XRD pattern of DASB (CCDC-271984).](image)

![Figure 5. FT-IR spectrum of the DASB crystal.](image)

Table 1. XRD datasheet for diffraction peaks of DASB.

| 2θ(deg.) | d(Å)  | hkl | 2θ(deg.) | d(Å)  | hkl |
|----------|-------|-----|----------|-------|-----|
| 11.727   | 7.504 | 110 | 19.839   | 4.471 | 0 0-4 |
| 12.871   | 6.823 | 111 | 21.976   | 4.041 | 0 23 |
| 15.12    | 5.855 | -112| 25.661   | 3.468 | 0 24 |
| 16.111   | 5.496 | 020 | 26.18    | 3.401 | -1 31 |
| 16.86    | 5.254 | 021 | 27.298   | 3.264 | -3-11 |
| 18.935   | 4.683 | 022 | 30.054   | 2.971 | 133 |

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specimen, which are 300 °C to 334 °C, 334 °C to 476 °C, and 476 °C to 800 °C, respectively. In the first stage, which may be due to the gasification of S. The rapid decomposition takes place after 334 °C and the mass loss was 53.54%, which corresponds to the decomposition of toluene. Finally, the weight of material was reduced by 9.05% from 476 °C to 800 °C. Figure 6 (b) is shown that there is a obvious endothermic peak at 284.1 °C, which can determine the melting point of the material. The melting point of DASB and some other organic crystals is summarised in table 3. One can seen that the DASB crystal is more stable than DAST, DSTMS, and other derivatives.

3.4. UV–vis-NIR analysis
Optical studies can help to understand the state of electron transition when light interacts with molecules. The UV–vis-NIR absorption spectra of 1 mm thick DASB crystal were recorded by U-4100 spectrophotometer in the range of 320–2000 nm. Figure 7 (a) is shown the absorption and transmission spectrum. The region where UV light is impervious is due to the absorption of UV light, including strong electron transition from the ground state to the excited state and the bonding orbital to the anti-bonding orbital. The optical cut-off wavelength of DASB crystal was found to be 393 nm which corresponds to $\pi-\pi^*$. The band gap energy at the cut-off wavelength

| No. | Peak (cm$^{-1}$) | Assignment                        |
|-----|-----------------|-----------------------------------|
| 1   | 1639.81         | C=C stretching vibrations         |
| 2   | 1383.20         | The aromatic ring of the chromophore |
| 3   | 3037.15         | The aromatic C–H stretching vibration |
| 4   | 1517.80         | Vibrations of the aromatic ring   |
| 5   | 1336.34         | Symmetrical bending vibrations of methyl groups |
| 6   | 1162.75         | Asymmetric stretching vibration character of SO$_3$ group |
| 7   | 991.61          | C–C and C–N stretching vibrations |

Table 3. Comparison of melting point of stilbazolium derivatives

| Crystal | Melting point (°C) | References |
|---------|--------------------|------------|
| DAST   | 256 ± 1            | [25]       |
| DSTMS  | 258 ± 1            | [17]       |
| DSDMS  | 267 ± 1            | [25]       |
| DSAS   | 272 ± 1            | [16]       |
| DSMAS  | 256 ± 1            | [16]       |
| DSSS   | 277 ± 1            | [21]       |
| DASC   | 281 ± 1            | [18]       |
| DASB   | 284 ± 1            | Present work |
was calculated using the following equation:

\[ E_g = \frac{hc}{\lambda_{\text{max}}} \]  

(1)

where \( h \) is the Planck constant, \( c \) is the velocity light, and \( \lambda \) is the cut-off wavelength of the DASB crystal. The calculated value of band gap energy was 3.16 eV. The optical absorption coefficient \( (\alpha) \) was determined by equation (2):

\[ \alpha = \frac{2.303A}{t} \]  

(2)

where \( A \) is the absorbance and \( t \) is the thickness of the crystal. The band gap energy of DASB crystal was estimated by plotting \( (\alpha h \nu)^2 \) versus photon energy \( (h \nu) \) and exploring a straight line in tangent part of the curve to the energy axis \( (\alpha h \nu)^2 = 0 \) as shown in figure 7(b). The band gap energy of the DASB crystal was estimated to be 2.99 eV. Compared with the theoretical value (3.16 eV), the actual value is relatively small, indicating that there are growth defects in the growth process of the crystal.

The extinction coefficient \( (\kappa) \) can be derived from the following equation (3)

\[ \kappa = \frac{\lambda \alpha}{4\pi} \]  

(3)

The variation curve of extinction coefficient \( (\kappa) \) with wavelength is shown in figure 7(c). From the graph, the extinction coefficient \( (\kappa) \) increase with an increase in wavelength.

The wide band gap energy (2.99 eV) of the DASB crystal indicates there exists large transmittance window in the visible region [26]. The relation between absorption coefficient and photo energy is very important for studying electron energy band structure and transition [27]. The plot of absorption coefficient and photo energy of DASB crystal is observed from figure 7(d). In term of spectrum, the low energy transmittance window associated with free carrier absorption that can be caused by the presence of free electrons and holes and DASB crystal has strong absorption capacity when the energy value of light is higher than 2.99 eV, which is can be classified as lattice absorption caused by ion vibration. Moreover, due to electron transition between valence and conduction band, the absorption can be attributed to the fundamental absorption of photons in the range of 4.43–5.00 eV.
3.5. Photoluminescence
In addition to providing physical information of materials at the molecular level, the photoluminescence (PL) of organic crystals can also be found in application in related fields of optics, including defects, energy band gaps, concentration of free carriers in electron energy bands, and electron states with defective structures. The emission spectrum was recorded in the wavelength region between 300 and 600 nm using in FluoroMax-4 luminescence spectrometer. Figure 8 is shown there exist two main peaks at 405 nm and 467 nm, respectively. Because of the $\pi-\pi^*$ transition and electronic transition of the aromatic ring, a purple light appeared at 405 nm \cite{19}. Another weak PL emission peak at 467 nm is caused by defect transitions which indicates the defects in DASB crystal. Thus, DASB crystal has violet emission, and it is likely to play a role in application of optoelectronic devices.

3.6. Second harmonic generation measurement
The fundamental cause of harmonic generation (SHG) is the nonlinear optical material. The nonlinearity of the crystal can also be determined by the generation of the second harmonic signal. In our study, the SHG signal of DASB crystal was measured to determine the nonlinearity. The SHG efficiency of DASB is determined by placing the same size DASB grain between two glass plates using 2 $\mu$m Q-switched laser. In the measurement process, the SHG signal is converted into a voltage signal. And the collected signal is displayed through a photomultiplier tube using an oscilloscope of type DS1052E. The SHG of the obtained DASB crystal is shown in figure 9. From the graph, the SHG efficiency of DASB crystal is about 3 times higher than that of KDP crystal.
The results indicate that DASB crystal has second-order nonlinear optical properties similar to those of organic pyridine crystals.

4. Conclusion

dimethylamino-\textsuperscript{N\textprime}′-methyl-4′-stilbazolium \textsuperscript{p}-bromobenzenesulfonate was synthesized and the single crystals with dimension of $3 \times 3 \times 1 \text{mm}^3$ were grown by SNM-SE for the first time. The powder x-ray diffraction study confirms that the crystalline quality is very good. The existence of function groups in DASB were verified by FT-IR. By TG-DTG analysis of decomposition stages, it was found that the melting point was 284 °C. The optical spectrum of the DASB crystal shows that it is highly transparent in Vis-NIR region and the cut-off wavelength is 393 nm, optical parameters such as the absorption coefficient ($\alpha$), extinction coefficient ($\epsilon$) were calculated and the band gap energy ($E_g$) was 2.99 eV using Tauc’s plot. Photoluminescence studies suggest that strong emission observed at 405 nm, indicating strong charge transfer in the molecule. The SHG test confirms that the NLO efficiency of the grown crystal is 3 times higher than that of KDP. All the results indicate that DSASB crystal is a potential material for nonlinear optics in THz application.

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