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Linear and Non-Linear Optical Properties of Environmentally Stable DASC Single Crystal

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Abstract: Organic nonlinear optical crystal N, N-dimethylamino-N'- methylstilbazolium p-chlorobenzenesulfonate (DASC) has been successfully grown from mixed solvent of methanol: acetonitrile (1:1) solution by adopting slow solvent evaporation technique. Single crystal and powder X-ray diffraction analysis was carried out and it shows that DASC crystal belongs to monoclinic structure with Cc space group. The optical absorption is studied by UV-Vis absorption spectra. Second-harmonic generation (SHG) of DASC crystal has been investigated using Kurtz and Perry technique.
Keywords: Organic compound; X-ray diffraction; Stilbazolium derivative; Nonlinear optical materials

Introduction

Terahertz (THz) technology has entered into an unprecedented revolutionary era with ever growing applications in biology and medicine, monitoring and spectroscopy in pharmaceutical industry and science, medical imaging, material spectroscopy and sensing, security, and high-data-rate communications. High power and reliable THz sources and high performance THz spectroscopy and imaging systems have been developed over the past few years making it possible to explore new areas in science and technology. Organic non-centrosymmetric nonlinear optical (NLO) crystals are attractive due to their superior NLO properties when compared to semiconductors and inorganic materials. THz spectrometers based on popular ionic organic crystal, 4-N,N-dimethylamino-4-methyl-stilbazolium tosylate (DAST) is now available commercially. Since DAST has few issues like hydration and undesired crystal morphology, there are attempts to replace it with derivatives of DAST with similar structure. So research has been initiated and with a minor modification of substituents on the counter anion with this strategy, considerable change the crystal structure and SHG activity of stilbazolium salts can be achieved. Various derivatives of DAST have been successfully synthesized, among them; N, N-dimethylamino-N'-methylstilbazolium p-chlorobenzenesulfonate (DASC) is the one which has DAST like structure, high NLO activity and free from hygroscopic nature [1, 2]. In this work, the growth and structural, optical and NLO properties of DASC single crystal have been investigated.

Synthesis & Crystal growth

DASC was prepared by metathesization of the 4-N,N-dimethylamino-N'-methylstilbazolium iodide (DMSI) salt with sodium p-chlorobenzenesulfonate. The metathesizaton reaction was carried out as follows: Initially, 0.732 g (2 mmol) of DMSI was dissolved in 100 ml of distilled water by heating and simultaneously 0.4292 g (2 mmol) of sodium p-chlorobenzenesulfonate was dissolved in 30 ml of water with continued heating. These two hot solutions were mixed and further heated for 30 minutes at 70° C and then cooled to room temperature. The reaction resulted in the appearance of a red precipitate and the left out aqueous sodium iodide was separated from the former by vacuum filtration. The purity of DASC was further improved by successive recrystallization [4]. Crystal growth was performed by preparing 3.35 g of DASC dissolved in 150 ml of mixed solvent of acetonitrile and methanol (1:1) at 40^{o} C. After a period of time the thin plate like crystals were grown and the photograph is shown in figure 1.

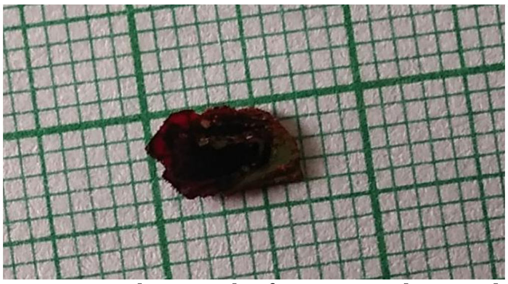


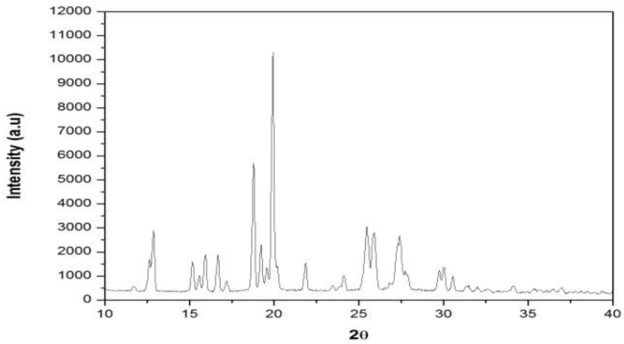
Figure 1 Photograph of DASC single crystal

Results& Discussions

Single crystal X-ray diffraction analysis

The crystallographic structure of DASC was determined via single X-ray diffraction analysis using a Bruker Kappa APEX II diffractometer. The structure was determined from the single crystal XRD; it is found that DASC single crystal belongs to *Monoclinic* Crystal system, with space group Cc. The unit cell parameters are a = 10.395Å, b = 11.201Å, c = 17.865 Å, $\alpha = 90^{o}$, $\beta = 92.06^{o}$, $\gamma = 90^{o}$ and Volume of 2081$Å^{3}$. Powdered sample of DASC was characterized by powder X-ray diffractometry at 1.506 Å using the Rigaku miniflex II X-ray diffractometer.

The sharp and well defined Bragg's peaks seen at specific 2θ angles (Figure 3.9) suggest the good crystallinity of the grown crystal.



Optical absorption analysis

Figure 2 shows the absorption spectrum of DASC recorded in solid phase between the wavelength region 200 to2100 nm. Since the DASC crystal is iso-structural to DAST one may not expect much deviation in the optical absorption property. DASC indicates strong absorption upto 700 nm, it correlating with the charge transfer process. This crystal is very transparent in higher wave lengths but at 1700 nm weak absorption observed for DASC crystal which is most probably due to the overtones of the C-H stretching vibrations. DASC shows weak absorption at 700-1600 nm which makes its potential candidate for NLO applications [5].

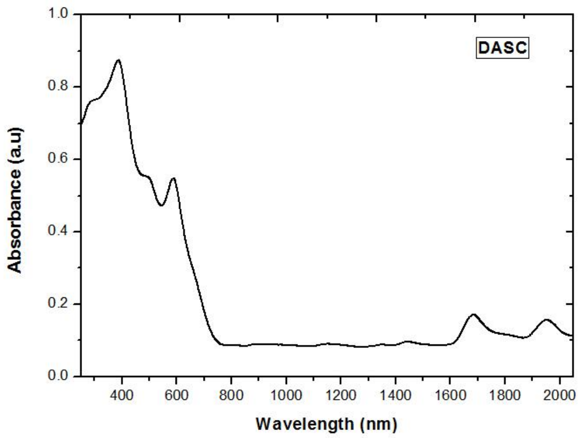


Figure 2 UV absorption spectrum of DASC crystal

NLO test-Kurtz and Perry powder SHG test

In order to find the NLO property, the grown crystal was subjected to SHG studies by Kurtz and Perry powder technique. The sample was ground into very fine powder and tightly packed in a microcapillary tube. The DAST crystal developed in our lab was taken as the reference material for comparison. The samples were then mounted in the path of a Q-switched Nd:YAG laser (1064 nm, Quanta ray series, Spectra Physics) beam of energy 10 ns pulse width and 0.68 J power. The generated SHG signal at 532 nm is split from the fundamental frequency using an IR separator. A detector connected to a power meter is used to detect the second harmonic intensity and read the energy input and output. The SHG signals recorded for the DASC and DAST crystals were nearly the same.

CONCLUSION

An efficient stilbazolium derivative crystal of DASC was successfully grown by slow evaporation technique. Single crystal X-ray diffraction analysis confirmed the noncentrosymmetric space group and the *monoclinic* structure and the powder XRD pattern confirms the very good crystallanity of the DASC single crystal. The optical absorption property was found for the developed material. SHG activity was ascertained by Kurtz and Perry powder technique. The observed optical properties make DASC as a potential material for NLO applications.

Acknowledgement

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