Growth, Spectral and Thermal Studies of Organic NLO Crystals of DSAS by SNM Technique

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Abstract. 4-N, N-dimethylamino-4’-N’- methyl- stilbazolium p-aminobenzenesulfonate (DSAS) single crystals were grown adopting slope nucleation method. Crystals of length 3 mm and diameter 0.5 mm were obtained successfully in 7 days. The elemental composition of DSAS was carried out by CHN analysis. The results are discussed in detail.

Keywords: NLO; NMR; Thermal

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INTRODUCTION

Organic non-centro symmetric materials offer vast design possibilities to tailor the linear and nonlinear properties, and owing to the almost completely electronic origin of the nonlinearity, they are well suited for future high speed devices. Waveguide structuring for integrated optics with organic crystals by photo bleaching, femtosecond, ablation, and ion implantation, as well as electro-optic modulation in thin organic single crystalline films and channel waveguides have been demonstrated. Recent research proves that the synthesis, crystal growth and characterization of a series of stilbazolium derivatives are possible by carefully modifying the structure with various substitutions on the counter-anion, expecting new molecules with high second-order optical nonlinearity. In this connection, 4-N,N-dimethylamino-4'-N'- methyl- stilbazolium p-aminobenzenesulfonate (DSAS), a stilbazolium chromophore based NLO material exhibits nearly equal NLO efficiency as that of 4-N,N-dimethylamino-4'-N'- methyl- stilbazolium iodide salt with the sodium p-aminobenzenesulfonate. The synthesized salt appeared green in colour. The purity of the product was further improved by successive recrystallization from methanol.

EXPERIMENTAL

Material synthesis

DSAS was synthesized by the condensation of 4-N,N-dimethylamino-4'-N'- methyl- stilbazolium iodide salt with the sodium p-aminobenzenesulfonate. The synthesized salt appeared green in colour. The purity of the product was further improved by successive recrystallization from methanol.

Crystal Growth

DSAS crystal was grown from slope nucleation method (SNM) by slowly evaporating solvent at room temperature. The SNM is a very simple and high yielding process. In this method, a Teflon plate with grooves is inserted (in slope shape) into the growth solution. The tiny spontaneous nuclei which are generated in the supersaturated solution are made to fall down onto the slope. As crystals grow larger, they slip downward along the slope until they arrive at one of the grooves. Finally, the crystals stand and then continue to grow larger on the groove. The beaker was sealed with a perforated lid and the solvent was allowed evaporate slowly. Teflon beaker was used in order to prevent the sticking of material to the side walls of the beaker during evaporation process. After 7 days, needle like crystals of length 3 mm and diameter 0.5 mm were obtained.
FIGURE 1. DSAS crystals grown by slope nucleation method

CHN analysis

The elemental composition of DSAS crystal was carried out by CHN analysis and the result is in good agreement with theoretically calculated and reported values (Table 1).

<table>
<thead>
<tr>
<th>TABLE 1. CHN analysis of DSAS</th>
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<tbody>
<tr>
<td>DSAS Formula</td>
</tr>
<tr>
<td>C_{22}H_{25}N_{3}O_{3}S</td>
</tr>
<tr>
<td>C %</td>
</tr>
<tr>
<td>H %</td>
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<tr>
<td>N %</td>
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NMR spectral analysis

The proton NMR spectrum of DSAS was recorded by dissolving the sample in deuterated methanol. In the proton NMR spectrum of DSAS, the singlets at 3.088 and 4.233 are assigned to six Hydrogens of N-(CH_{3})_{2} and three hydrogens of N-CH_{3} respectively. The singlet at 4.868 is due to two hydrogens of NH_{2} in the anion. The doublets at 6.665 and 7.558 are due to the two aromatic hydrogens ortho to −SO_{3} and two aromatic hydrogens ortho to −NH_{2}. The doublets at 6.801 and 7.62 are due to the four hydrogens of the N-(CH_{3})_{2}C_{6}H_{4} aromatic ring. The doublets at 7.985 and 8.523 are due the four hydrogens to the C_{6}H_{4}N aromatic ring. The doublets at 7.122 and 7.867 are due to the two olibinic hydrogens (HC=CH). The multiplet observed at 3.33 is due to the solvent (CD_{3}OD).

TG/DSC studies

The thermogravimetric analysis of DSAS was recorded between 30 and 830°C in nitrogen atmosphere at a scanning rate of 20 K/min by TG analyzer Q500 V20 Build 36. The TG/DTG and DSC traces are shown in Figures 2 and 3. It is infer from TG/DTG trace, DSAS crystal exhibit the two stages of decomposition. The maximum weight loss of DSAS is found to occur at the first stage of decomposition. The melting point of DSAS crystal is noted at 228.9 °C from the DSC trace. Hence, from this study it is concluded that the applicability of this material to NLO is limited to maximum temperature of 228.9 °C.

CONCLUSION

Organic NLO crystal of DSAS was grown by SNM technique. Elements of DSAS were determined by CHN analysis. Functional groups of the grown crystal were confirmed from the NMR studies. Thermograms reveal that the DSAS crystal thermally stable upto 228.9 °C.

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REFERENCES
