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Growth and spectroscopic analysis of semi-organic bisthiourea sodium fluoride crystal

V. Krishnakumar *, L. Guru Prasad

Department of Physics, Periyar University, Salem-636 011, India

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ABSTRACT

A semi-organic bisthiourea sodium fluoride (BTSF) is synthesized at ambient temperature and the single crystal of bisthiourea sodium fluoride is grown in slow evaporation technique using water as solvent. The cell parameters of the grown crystal are estimated from single crystal XRD analysis and also unambiguous assignments of fundamental modes of various molecular groups are made from the recorded FTIR and FT-Raman spectra. The thermal stability of the grown crystal is investigated using thermo-gravimetric analysis studies. Optical transmittance percentage of the grown crystal is measured from UV–VIS studies.

1. Introduction

In recent past, more emphasis has been given by scientists to develop semi-organic crystals. Semi-organics are the type of compounds that have the advantages of both organic and inorganic materials. Metal organic complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the coordinated metal centre [1]. Thiourea molecules can be co-ordinates with metal ions to form a stable co-ordinate complex, which can be crystallized either by solution growth technique or by gel growth technique [2]. Thiourea, a centrosymmetric molecule, which on coordination with a metal ion gives a non-centrosymmetric material [3]. Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds [4].

In this work, we report detailed studies about the growth, structural, vibrational, thermal and optical properties of BTSF crystal.

2. Experimental procedure

2.1. Synthesis

BTSF is synthesized by mixing thiourea (99%, Merck) and NaF (98%, Himedia) in the ratio of 2:1 in double distilled water. Since thiourea has the coordination capacity to form different phases of metal–thiourea complexes, the mixtures of the reactants are stirred well to avoid co-precipitation of multiple phases. This yields the BTSF complex, which is further purified by recrystallization process.

$$NaF + 2CS(NH_2)_2 \rightarrow Na[CS(NH_2)_2]_2F$$

2.2. Crystal growth

Single crystal of BTSF is grown in slow evaporation technique at room temperature using water as solvent. The supersaturated solution of BTSF is prepared in known amount of double distilled water. This is kept at room temperature and optimally closed for controlled evaporation. After the period of 7–10 days, colorless, transparent crystals are obtained. The size of one such grown crystal is $7\times5\times8$ mm^3 and is shown in Fig. 1.

3. Results and discussion

3.1. Single crystal XRD

The cell parameters of the grown crystal are obtained using single crystal XRD with Bruker platform diffractometer (graphite monochromated, MoK alpha = 0.71073 Å). It is observed that the BTSF crystal belongs to orthorhombic system with the cell parameters a = 6.493 Å, b = 7.914 Å and c = 9.606 Å with $\alpha=\beta=\gamma=90°$. The calculated cell volume is 493.610 Å^3.

3.2. Vibrational analysis

The vibration analysis of the grown BTSF crystal is done using FTIR and FT-Raman spectrum. The FTIR spectrum is recorded in the range of 400–4000 cm^{-1} using Brucker IF S66V spectrometer. The FT-Raman spectrum is recorded in the range of 40–4000 cm^{-1} using Brucker FRA 106 spectrometer. The recorded spectrums are shown in Figs. 2 and 3 respectively.

In FTIR, the NH stretching vibrational bands are observed at 3366 and 3163 cm^{-1} since these vibrational bands are not shifted to lower frequencies [5–12], it is confirmed that the bonding must be between Na–S atoms. The greater double bond character of C–N on the formation of BTSF is observed from the N–C–N stretching band at 1468 cm^{-1} [3].

* Corresponding author. Tel.: +91 427 2345766x246; fax: +91 427 2345565.
E-mail addresses: vkrishna_kumar@yahoo.com (V. Krishnakumar), guruphysics@gmail.com (L. Guru Prasad).

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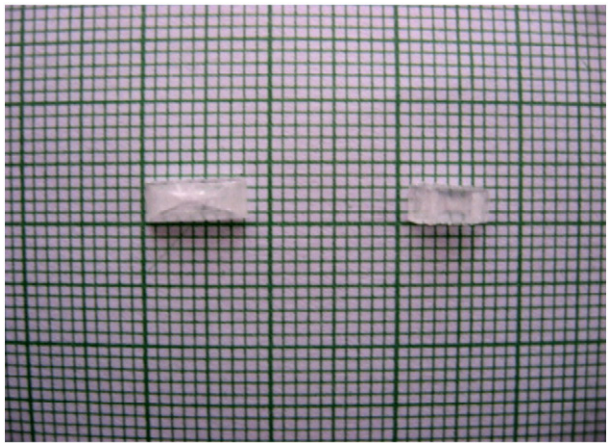

Fig. 1. Photograph of solution grown BTSF.

Thiourea can co-ordinate with metal through S or N atom. If the bonding is through sulfur, there will be decrease in CS stretching frequency and an increase in CN stretching frequency. The reverse happens if it is through nitrogen [6]. From the FTIR, it is observed that the CS stretching vibrations is shifted to 1381 cm^{-1} from 1412 cm^{-1}. However, the CN stretching vibration is shifted to 1092 cm^{-1} from 1089 cm^{-1} and the same is observed at 1095 cm^{-1} in Raman spectrum. This again conforms the formation of metal sulfur bond. The stretching mode of CS bands is observed at 730 and 733 cm^{-1} in FTIR and FT-Raman respectively and the rocking mode of CS vibrations is observed in Raman at 443 cm^{-1}. It is observed that the low-frequency vibrations are more active in Raman spectra.

3.3. Thermal analysis

The TGA/DTA spectrum of BTSF is recorded using SDT Q600 V8.3 instrument with the heating rate of 20 °C/min in air atmosphere and is shown in Fig. 4. In TGA, it is observed that there is no weight loss up to 180 °C. Which shows the absence of physically adsorbed or lattice water in the crystal. The DTA curve in Fig. 4 shows an exothermic peak at 174 °C and the corresponding TGA curve shows no weight loss and hence this can be regards as the melting point of the BTSF [13]. It is observed that the BTSF decomposes into two stages. First stage occurs at 180 °C and the weight loss is 80%. This is due to the loss of thiourea molecules. Second stage starts at 236 °C and the

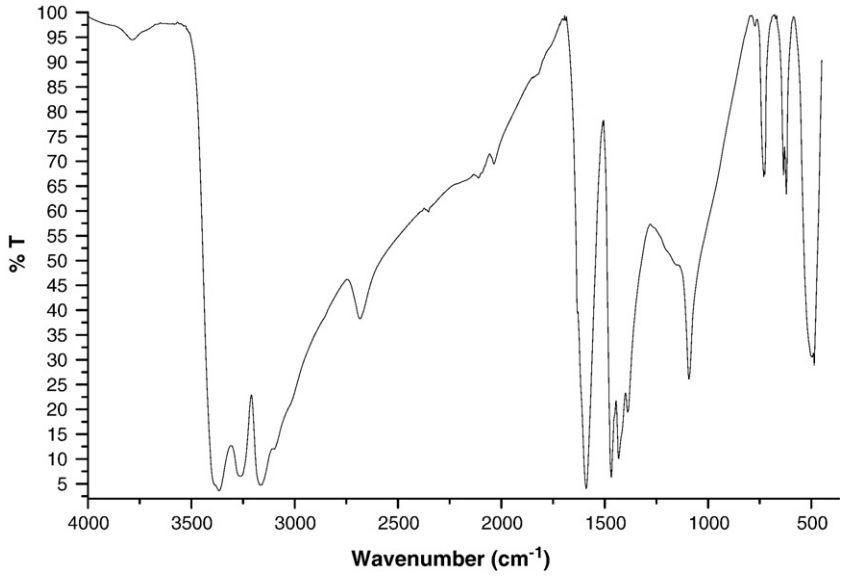

Fig. 2. FTIR spectrum of BTSF.

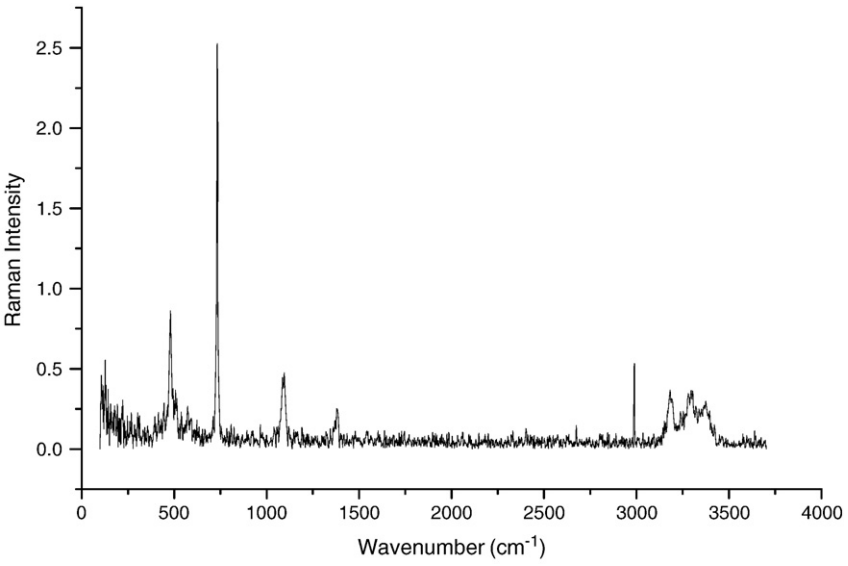

Fig. 3. FTRaman spectrum of BTSF.