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Investigation on the growth and characterization of nonlinear optical single crystal of bis thiourea iron(II) sulphate

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Abstract Single crystal of bisthiourea iron(II) sulphate was grown by slow evaporation technique at 303 K. The structural properties of the grown crystals were characterized by FTIR spectroscopy, UV spectroscopy and powder X-ray diffraction. FTIR and UV spectra provide information about the presence of functional groups. Thermal analysis confirms the crystal is thermally stable up to 167.02 °C.

Keywords Bisthiourea iron(II) sulphate · Slow evaporation · UV · FTIR · Thermal analysis

Introduction

Thiourea, a centrosymmetric molecule forms non-centrosymmetric complexes by co-ordinating different metal ions leading to nonlinear optical properties. Crystallization of semiorganic materials for use in nonlinear optical (NLO) devices is of great interest due to their high nonlinearity, high flexibility interims of molecular structure, high optical damage threshold and low cost [1–8]. Single crystals of bisthiourea iron(II) sulphate (hereafter abbreviated as BITS) are being used extensively and have vast demand in electronic industry as polarization filter, electronic light shutter, electronic modulator, optical voltmeter and on elements of electro-optic and electro acoustic devices [9]. The origin of nonlinearity in NLO materials arises due to the presence of delocalized π electrons in BTIS in connecting donor and acceptor groups responsible for enhancing their asymmetric polarisability [10]. BTIS also exhibit pyroelectric effect, which is utilized in IR, UV, and XRD detection and infrared imaging.

A transition metal has an incomplete *d*-subshell; it can give rise to cations with an incomplete *d* subshell. All the transition metals (including Fe^{2+}) have the same arrangement of outer electrons and only 3*d* orbitals lower down are different. The incorporation of transition metal in the crystalline matrix will generally influence the physical properties [11–14]. In recent years, some materials doped with the transition metal, tetrahedral Co(II) have been reported and it is interesting to observe excellent absorption, emission [15], and magnetic properties. The cobalt oxide additions in the $ZnO–Bi_2O_3$ based varistors improve the nonlinear properties [7]. It is interesting to observe that the superconduction transition temperature (Tc) in YBCO single crystal is considerably enhanced by cobalt doping [4, 5], as recently investigated. Thermal and spectral analyses are very useful methods for materials characterization. Therefore, many authors have used these techniques for various materials characterization [16–36]. As a continuation of our previous studies BTIS were grown by slow evaporation technique at room temperature.

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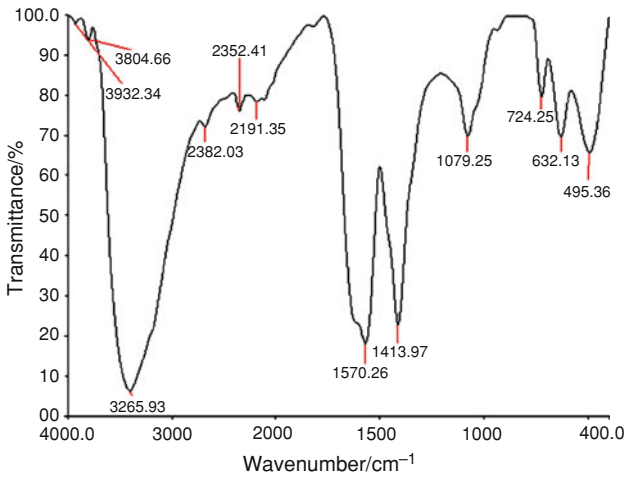

Fig. 1 FTIR spectrum of bisthiourea iron(II) sulphate

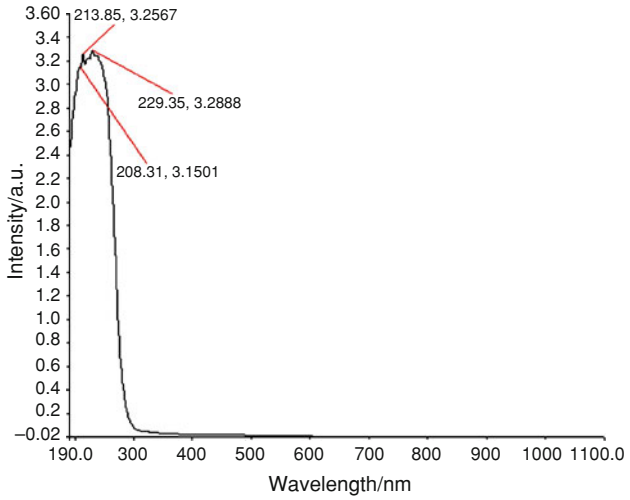

Fig. 2 UV spectrum of bisthiourea iron(II) sulphate

Experimental details

Ferrous sulphate was mixed with Analar grade thiourea in 1:2 stoichiometric ratio with double distilled water. The reaction mixture was heated over a water bath till the ferrous sulphate and thiourea dissolves to form a clear solution. Undissolved material was removed through a Whatmann filter paper and filtrate is collected into a clear dry beaker.

$$FeSO_4 + 2(NH_2)_2C = S \rightarrow \{Fe\left[(NH_2)_2C = S\right]_2\}SO_4$$

And then tightly covered saturated solution with a perforated paper was kept in a constant temperature bath. The content of the solution was filtered and the crystallization took place within 2 weeks.

Measurements

The FTIR spectra were recorded on an AVATAR 330 FTIR by KBr pellet technique. The UV spectrum was performed on a UV double beam spectrophotometer in the spectral range 190–1,100 nm. The Kurtz powder SHG instrument was used for testing SHG.

Results and discussions

FTIR spectral analysis

The FTIR spectra of BTIS are given in Fig. 1. The characteristic vibrational frequencies of pure thiourea [5] and BTIS are very similar. However, for heavily doped Fe(II) specimen some vibrational changes have been noticed in

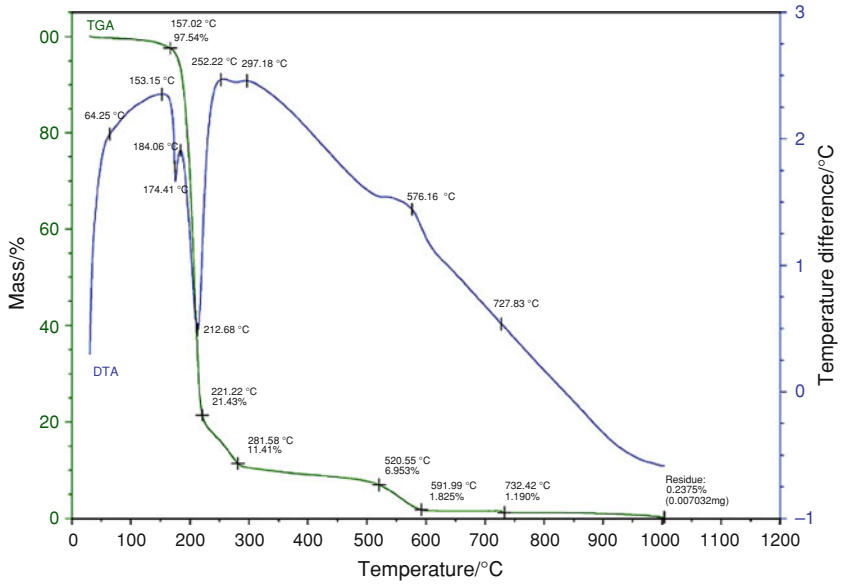

Fig. 3 TG–DTA of bisthiourea iron(II) sulphate

FTIR spectra. The symmetric asymmetric C=S stretching vibrations at 740 and 1,417 cm^{-1} of thiourea are shifted to lower frequencies 724.25 and 1,413.97 cm^{-1} in the FTIR spectra. The band at 1413.97 cm^{-1} is assigned to –N=C=N– stretching vibrations of BTIS. The heavily doped Fe(II) spectrum indicates some distortion of lattice as a result of incorporation of Fe(II) into the bisthiourea crystalline matrix.

UV spectral analysis

The UV spectra for BTIS are shown in Fig. 2. In BTIS, the π–π^* absorption band shifted to lower wavelength compared to thiourea. This is because of the formation BTIS complex decreases the bond length of C=S and thus longer energy required for this transition and hence absorption shows the blue end of the spectrum.

Thermal analysis

The TG–DTA curves of BTIS are shown in Fig. 3. The TG curve indicates a two step mass loss on heating the compound between 0 to 1,200 °C.

The following decomposition pattern is formulated for BTIS.

Step 1

$$[H_2N{-}CS{-}NH_2 \rightarrow Fe \leftarrow H_2N{-}CS{-}NH_2]SO_4 \rightarrow 2FeSO_4 + 2NH_3 + CS_2$$

$$H_2N{-}CS{-}NH_{2\ldots}S = C{-}(NH_2)_2 \rightarrow 2NH_3 + CS_2 + C + S.$$

Two molecules of ammonia, ferrous sulphate, and carbon disulphide are lost on heating the compound from 167.02 to 281.58 °C. This accounts for 97.54% mass loss observed in TG curve. The remaining portion of BTIS slowly decomposed from 520.55C to 591.99 °C. Above 167.02 °C thiourea in BTIS decomposes into two molecules of ammonia and ferrous sulphate. Afterwards, thiourea in BTIS begins to split to two molecules of ammonia and CS_2. This accounts for 1.825% mass loss observed in the TG curve. The thermogravimetric study thus confirms the formation of title compound in the stoichiometric ratio and the decomposition pattern of UTIS. The DTA curve presented in Fig. 3 shows an endothermic peak at 212.68 °C corresponds to the first stage decomposition.

Conclusions

Single crystals of BTIS with appropriate size were grown by slow evaporation technique in room temperature for the first time. The FTIR spectral studies confirm the presence of functional groups in BTIS. The UV spectrum confirms the formation of BTIS complex. Thermal studies reveal that the melting point of the sample is 167.02 °C, which is higher than other complexes.

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