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Growth and characterization of tris thiourea chromium(III) sulphate

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Abstract Single crystal of tris thiourea chromium(III) 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 analysis. FTIR and UV spectra provide information about the presence of functional groups. Thermal analysis confirms that the crystal is thermally stable up to 163.48 °C. The TG curve presented a two-step mass loss on heating the compound at 0–1,200 °C.

Keywords Tris thiourea chromium(III) sulphate · Slow evaporation · UV · FTIR · TG · DTA

Introduction

Chromium tris thiourea sulphate (TTCS) is a metal organic nonlinear optical crystal which can be grown fairly and easily in large sizes from aqueous solution. Its growth and characterization have been reported in a number of recent publications [1–8]. Good quality tris thiourea chromium III sulphate were grown, and characterization studies such as UV, TG–DTA, FTIR, AC conductivity, NLO properties etc., have been performed and discussed in detail in this paper. The thiourea crystals are being used extensively and have vast demand in the electronic industry as polarization filter, electronic light shutter, electronic modulator, optical voltmeter and as elements of electro-optical and electro-acoustic devices. The origin of non linearity in NLO materials arises due to the presence of delocalized π-electron system connecting donor and acceptor groups, and responsible for enhancing their asymmetric polarizability [9–15]. Thiourea crystals also exhibit pyroelectric effect which is utilized in infrared (IR) and ultraviolet (UV), scanning electron microscope (SEM) detection and infrared imaging. Thermal and spectral analyses are very useful methods for materials' characterization. Therefore, many authors have applied these techniques for many materials characterization [16–36].

Materials and methods

TTCS was synthesized by dissolving thiourea and chromium III sulphate in 3:1 ratio in doubled distilled water, the saturated solution of thiourea with dopants was prepared using the deionized water at 30 °C in an air tight container and heated to a few degree above the saturation temperature to enable homogenization of the solution. Constant stirring of the solutions was employed to overcome the concentration gradient in the crystallizer.

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Distinguished with above said dopants, crystals were grown from saturated solution by solvent evaporation at 30 °C using a constant temperature bath having control accuracy of 0.01 °C. Good quality crystals were obtained after 2 weeks.

Results and discussions

FTIR spectral analysis

The FTIR spectra of TTCS are given in Fig. 1. The characteristic vibrational frequency of pure thiourea and TTCS are very similar. However, for heavily doped chromium(III) sulphate, some vibrational changes have been noticed in FTIR spectrum. The symmetric and asymmetric C=S stretching vibrations at 740 of thiourea is shifted to lower frequency (729.23) in the FTIR spectrum. The band at 1418.86 is assigned to N–C–N stretching vibration of BTCS. The heavily doped Cr(III) spectrum indicates some distortion lattice as a result of Cr(III) into the tris thiourea crystalline matrix.

UV spectra analysis

The UV spectra of thiourea and TTCS are shown in Fig. 2. In TTCS, the π–π* transition shifted to lower wavelength (234.01) compared to thiourea. This is because of the formation of TTCS complex, decreases the bond length of C=S, and thus larger energy required for this transition and hence absorption shows the blue end of the spectrum.

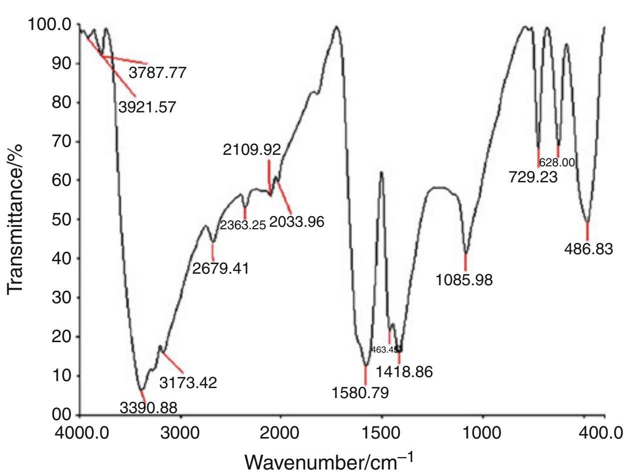


Fig. 1 FTIR spectrum of tris thiourea chromium(III) sulphate

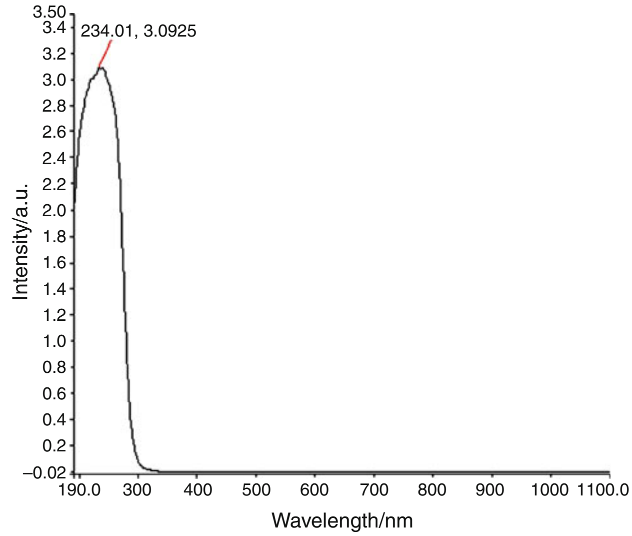


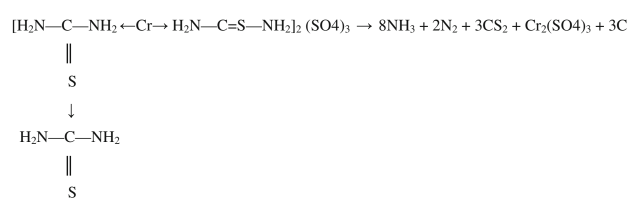
Fig. 2 UV spectrum of tris thiourea chromium(III) sulphate

Thermal analysis

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

The following decomposition pattern is formulated for TTCS.

Step 1



Step 2

$$2Cr_2(SO_4)_3 \rightarrow 2Cr_2O_3 + 6SO_2 + 3O_2$$

Eight molecules of ammonia and three molecules of CS_2 are lost on heating the compound from 163.46 to 274.19 °C. This accounts to 81.54% of mass loss observed in the TG curve. The remaining portion of TTCS (chromium III sulphate) slowly decomposes from 479.90 to 571.05 °C. Thiourea changes to NH_4SCN at 270 °C. The final solid product is melon $C_6H_3N_9$, which decompose to $(CN)_2$, NH_3 and N_2. Afterwards, chromium(III) sulphate begins to split to $2Cr_2O_3$, $6SO_2$ and $3O_2$. The TG study thus confirms the formation of title compound in the

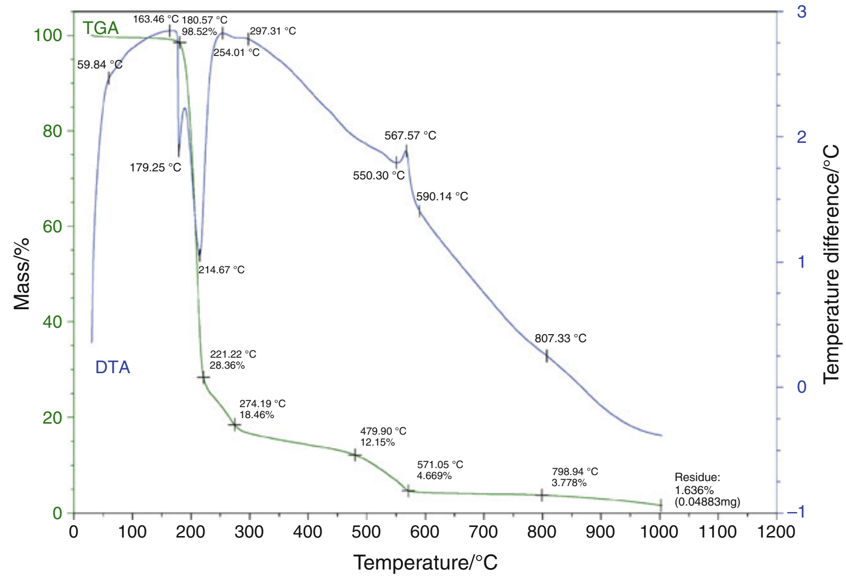


Fig. 3 TG-DTA curves of tris thiourea chromium(III) sulphate

Table 1 Dielectric constant at various temperature and frequencies

Temperature/°C	20 Hz	100 Hz	1 kHz	10 kHz	100 kHz	1 MHz
100	11299.93	5219.77	3826.64	3223.35	2893.84	2707.28
90	10433.73	4921.76	3697.01	3194.27	2878.09	2698.80
80	10141.78	4641.92	3629.17	3124.01	2829.64	2679.42
70	8397.33	4285.76	3581.93	3012.56	2672.15	1980.43
60	7102.32	4089.51	3303.30	2926.55	2620.06	1917.43
50	6423.92	3346.91	2801.77	2348.70	2203.33	2087.03
40	4352.39	2765.43	2586.14	2280.86	2168.20	1905.32

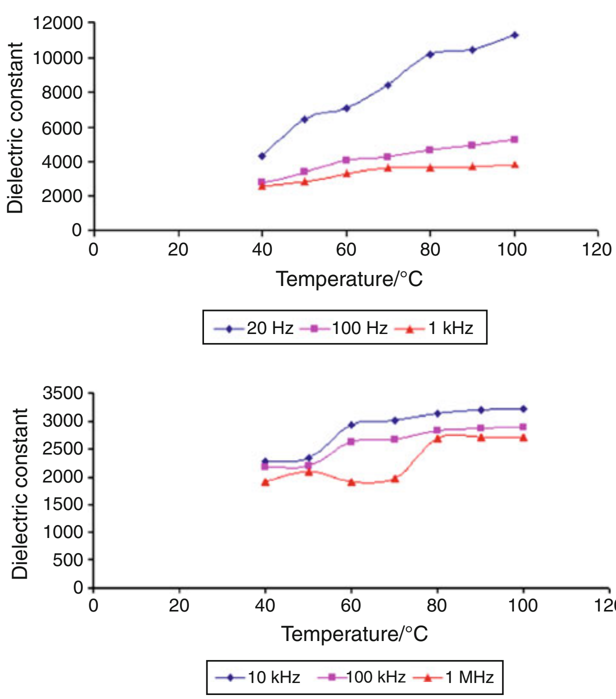


Fig. 4 Dielectric constant at various temperature and frequencies

stoichiometric ratio and decomposition pattern of TTCS. The DTA curve in Fig. 3 shows an endothermic peak at 214.6 °C corresponds to the first stage decomposition of TTCS.

X-ray diffraction studies

The single crystals of TTCS have been subjected to X-ray diffraction studies on an ENRAF NONIUS CAD4 X-ray diffractometer to determine the unit cell dimension and morphology. The unit cell dimensions are $a = 5.4881$ Å, $b = 7.6620$ Å and $c = 8.5495$ Å and Volume = 359.5066 Å^3. The crystal belongs to orthorhombic system.

Dielectric studies

The dielectric constant (ε_r) values obtained in the present study are provided in Table 1. The variation with temperature of ε_r value obtained in the present study is shown in the Fig. 4. It can be seen that the ε_r value increases with the

Table 2 Conductivity of tris thiourea chromium sulphate at various temperature and frequencies

Temperature/°C	20 Hz	100 Hz	1 kHz	10 kHz	100 kHz	1 MHz
100	5.317	6.939	32.356	102.286	611.724	3162.644
90	4.016	5.749	27.763	92.400	576.374	2972.581
80	2.843	4.828	25.841	88.629	480.096	2712.751
70	1.933	3.170	12.752	82.116	401.349	1872.864
60	1.035	2.843	21.315	70.003	364.375	1279.966
50	0.693	1.712	13.247	44.233	257.393	1393.181
40	0.203	1.230	10.358	29.182	217.104	1059.902

Table 3 Dielectric loss at various temperature and frequencies

Temperature/°C	20 Hz	100 Hz	1 kHz	10 kHz	100 kHz	1 MHz
100	0.423	0.239	0.152	0.057	0.038	0.021
90	0.346	0.210	0.135	0.052	0.036	0.019
80	0.252	0.187	0.128	0.051	0.030	0.182
70	0.207	0.133	0.116	0.049	0.027	0.017
60	0.131	0.125	0.085	0.043	0.025	0.015
50	0.097	0.092	0.072	0.034	0.021	0.012
40	0.042	0.080	0.064	0.023	0.018	0.010

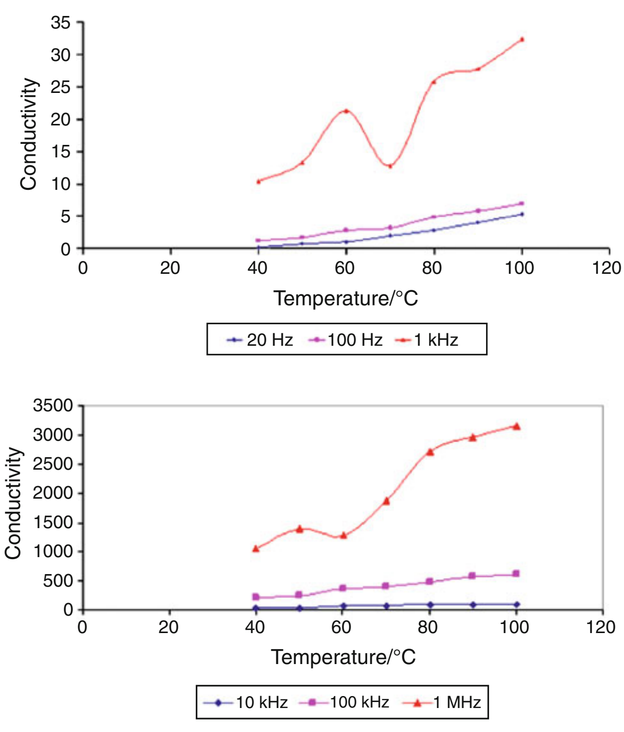


Fig. 5 Conductivity at various temperature and frequencies

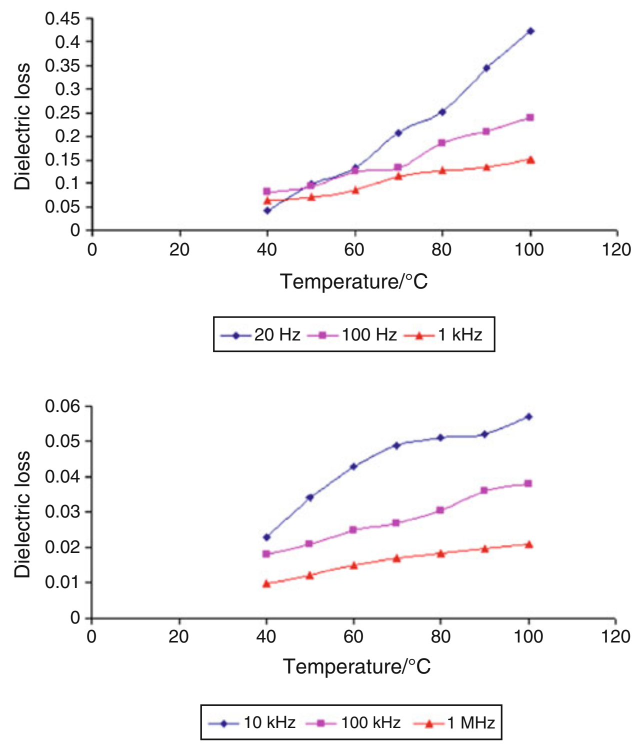


Fig. 6 Dielectric loss at various temperature and frequencies

increase in temperatures for various frequencies. The tan δ and σ_{ac} values obtained in the present study are provided in Tables 2 and 3 and also shown in the Figs. 5 and 6, respectively. These values also vary with temperature for various frequencies in a similar way as that for the dielectric constant.

Conclusions

Single crystals of TTCS 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 TTCS. The UV spectrum confirms the formation of TTCS complex. Thermal studies reveal that the melting point of the sample is 163.48 °C. The TG curve confirms a two-step mass loss on heating the TTCS at 0–1,200 °C. The TG study also confirms the formation of title compound in the stoichiometric ratio and decomposition pattern of TTCS. The DTA curve shows an endothermic peak at 214.6 °C corresponds to the first stage decomposition of TTCS.

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