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Growth and characterization of tris-thiourea strontium chloride single crystals

H.O.Jethva[1]*, R.R.Hajiyani[2]

[1]Department of Physics, M. M. Science College, Morbi - 363 642, (INDIA)

[2]Forensic Science Laboratory, Gandhinagar, (INDIA)

E-mail: hojethva@rediffmail.com

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ABSTRACT

Tris-thiourea strontium chloride was synthesized and single crystals were grown by the slow solvent evaporation technique using aqueous solvent. The solubility curve was obtained as well as the grown crystals were characterized by thermo-gravimetric analysis. Applying Coats and Redferm relation to the thermo-gram the kinetic and thermodynamic parameters were calculated.

KEYWORDS

Tris thiourea strontium chloride;
TGA;
Solubility curve.

INTRODUCTION

Nonlinear optical materials crystals are of considerable interest because of their various applications in science and technology, such as different harmonic generators, sum and difference generators and parametric oscillators[1,2]. The inorganic and organic class of NLO materials are available with different merits and demerits[3,4]. The another class of NLO materials are the semi-organic materials, which possess the properties of both organic and inorganic NLO materials[5-7]. Metal complexes of urea and urea analogous have been explored[7]. Bis-thiourea cadmium chloride[8] and bis-thiourea zinc chloride[9] crystals have been grown and characterized, which exhibit good NLO properties.

In the present study an attempt is made to synthesize tris-thiourea strontium chloride (TTSC) and grow single crystal by slow solvent evaporation method. The grown crystals were characterized by TGA and EDAX study. However, at present the study of NLO properties was not carried out.

EXPERIMENTAL

Pure TTSC salt was synthesized by slow solvent evaporation method using AR grade thiourea and strontium chloride in double distilled water. The expected chemical reaction was

$$SrCl_2 + 3\,CS(NH_2)_2 \rightarrow [Sr(NH_2CSNH_2)_3]\,Cl_2$$

The synthesized salt was purified by several time re-crystallizations. TTSC single crystals were grown by slow evaporation technique at room temperature. The growth vessel was closed and through a small opening slow evaporation was allowed. A constant temperature water bath with $\pm 0.1^{o}C$ accuracy was used to maintain the constant temperature. Crystal growth was completed in about 10 days. In the present investigation, the growth of TTSC single crystals by slow evapora-

tion technique at room temperature and its characterization by using TGA and solubility curve are reported.

RESULTS AND DISCUSSION

TGA study

Figure 1 shows the thermo-gram of TTSC.

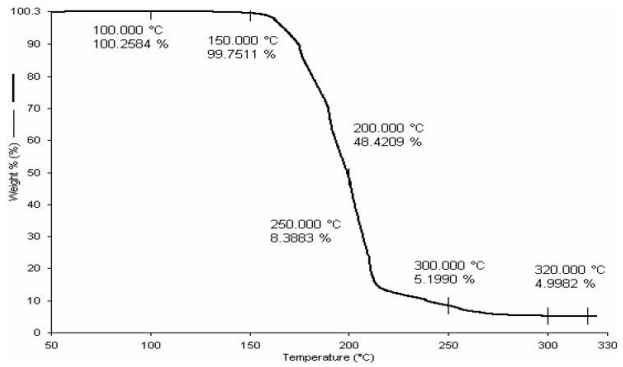

Figure 1

The thermo-gram indicates that the compound is stable approximately up to 160 °C. Then the decomposition starts and a stable state are achieved from approximately 270 °C to the end of the analysis, where the loss of about 96% of the original mass is observed. The end product is expected as metallic residue of strontium.

Kinetic and thermodynamic study

The use of thermo-gravimetric data to evaluate the kinetic parameters of solid-state reactions involving weight loss has been investigated by many workers[10-13]. If the pyrolysis occurs through a many stepped mechanism, usually, the shape of the curve can be determined by the kinetic parameters of pyrolysis, such as order of reaction, frequency factor and energy of activation. Kotru et al.[14] reported the kinetics of solid state decomposition of neodymium tartrate. Recently, the kinetics of dehydration of gypsum[15], lithium sulphate monohydrate single crystals[16] as well as the kinetic and thermodynamic parameters of decomposition of chromate in different gas atmosphere[17] and L-arginine doped KDP crystals[18] has been evaluated.

Usually, the kinetic parameters can be evaluated from the TG curves by applying several equations[11-13,19], which are proposed by different authors on the basis of different assumptions to the kinetics of the reaction and the Arrhenius law. These equations are the Coats and Redfern relation, the Horowitz and Metzger relation and the Freeman and Carroll relation. However, in the present investigation, the Coats and Redfern relation is discussed in detail because it facilitates not only to evaluate the activation energy and order of reaction but also the frequency factor.

Coats and redfern (C-R) relation

Coats and Redfern[10] derived the following equation to determine the values of activation energy and order of reaction.

$$\log_{10}\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right) = \left\{\log_{10}\left(\frac{AR}{\alpha E}\right)\left(1-\frac{2RT}{E}\right)\right\} - \left\{\frac{E}{2.3RT}\right\} \quad (1)$$

Where E is the activation energy of the reaction, A is the frequency factor, α is the fraction of decomposed material at temperature t, n is the order of reaction and T is the absolute temperature. The plot of $Y = -\log_{10}\left(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right)$ versus $X = \frac{1}{T}$ were straight line for different values of n. The value of activation energy is obtained from the slope of the best linear fit plot. The frequency factor can be calculated for a particular temperature using relation (1). The Coats and Redefrn relation was solved for various values of n. The statistical regression analysis was applied to different values of n and the highest values of co-relation coefficient indicated the best linear fit curve. This was found

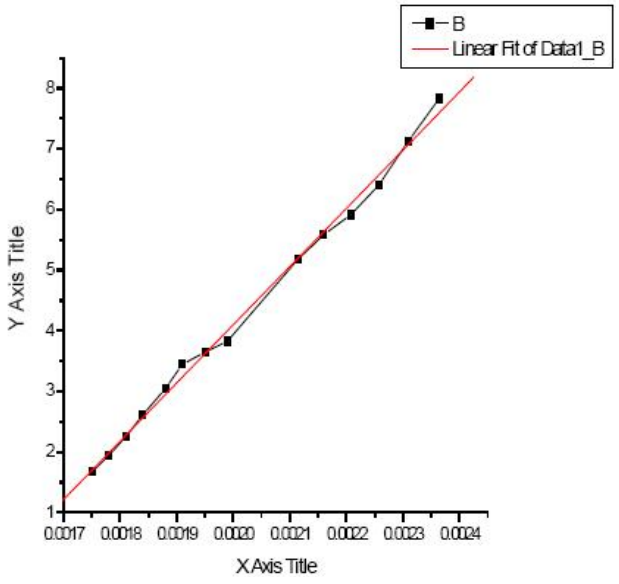

Figure 2

for n = 2.5. Figure 2 shows the plot drawn for Coats and Redfern relation.

The values of activation energy, frequency factor and the order of reaction are indicated in the following TABLE 1.

TABLE 1 : The values of different kinetic parameters of TTSC obtained from the coats and redfern relation

Order of Reaction (n)	Activation Energy (E) kJ/Mol	Frequency Factor (A)
2.5	183.8	5.121×10^{30}

Thermodynamic parameters

The thermodynamic parameters have been evaluated for the grown TTSC crystals. Different thermodynamic parameters such as the standard entropy of activation ($\Delta^{\#}S^{o}$), standard enthalpy ($\Delta^{\#}H^{o}$), standard Gibbs free energy ($\Delta^{\#}G^{o}$) and standard change in internal energy ($\Delta^{\#}U^{o}$) were calculated by applying well known formulae, as described in detail by Laidler[20]. The thermodynamic parameters for dehydration of gel grown iron (II) tartrate have been estimated by Joseph at el. Dabhi and Joshi[21,22] have reported the thermodynamic parameters for dehydration of various gel grown metal-tartrate crystals and Parikh et al[18].

The following TABLE 2 summarizes the values of different thermodynamic parameters obtained for decomposition of TTSC crystalline sample. Positive values of $\Delta^{\#}S^{o}$ and $\Delta^{\#}H^{o}$ suggest that the process is spontaneous at high temperatures. Positive value of $\Delta^{\#}G^{o}$ suggests that the samples are thermodynamically unstable.

TABLE 2 : The values of different thermodynamic parameters of TTSC crystals

Standard Entropy ($\Delta^{\#}S^{o}$) kJ/Mol	Standard Enthalpy ($\Delta^{\#}H^{o}$) kJ/Mol	Standard Gibbs Free Energy ($\Delta^{\#}G^{o}$) kJ/Mol	Standard change in Internal energy ($\Delta^{\#}U^{o}$) kJ/Mol
0.3390	175.94	15.6	179.88

Solubility determination and solubility curve

The solubility of the synthesized TTSC was determined gravimetrically in suitable solvent at different temperatures and the solubility curve was drawn by taking temperature (^{o}C) along X-axis and the solubility (gm/cc) along Y-axis, which is as shown in the following figure 3.

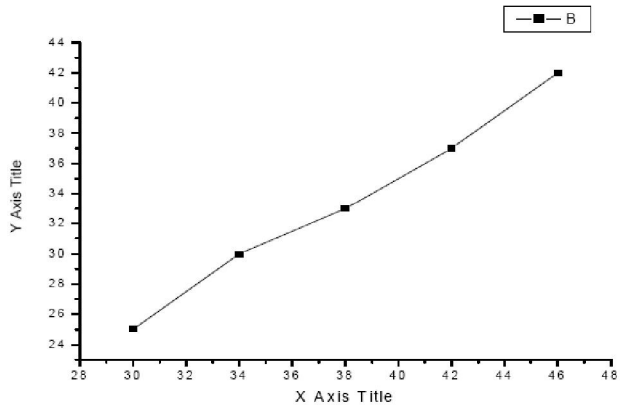

Figure 3

The nature of this curve provides important information of solubility of solute at different temperatures and the conditions required to be maintained to grow crystals. The solubility of TTSC increases with temperature.

CONCLUSION

The TTSC crystals were grown by slow solvent evaporation technique. The thermo-gram of the TTSC indicated that the compound was stable up to 160 ^{o}C. Then the decomposition starts and a stable state are achieved at 270 ^{o}C to the end of the analysis, where the loss of about 96% of the original mass is observed. Kinetic and thermodynamic parameters were evaluated suggesting a spontaneous process. The solubility of the TTSC increased with temperature.

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