Growth and Thermogravimetric Analysis of ferrous, barium and ammonium chloride doped Zinc (tris) Thiourea Sulfate (ZTS) crystals

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Abstract: Among all materials crystals play an important role in recent market. The technological development of a nation is largely dependent on the device fabrication based on crystalline solids. Single crystals find prudent place in modern devices like transistors, rectifiers, polarize lasers, modulators, computer memory, strain gauge, etc. So, crystal growth studies of large and apparently perfect crystals of many materials in nature have been a subject of considerable concern to many scientists[1]. Zinc tris-Thiourea Sulfate (ZTS) crystals have advantages of both organic and inorganic materials[2]. Ferrous chloride, barium chloride and ammonium chloride doped ZTS crystals were grown by single diffusion gel growth technique. Doped ZTS crystals were transparent. For the thermal analysis, Thermogravimetric Analysis (TGA) was done for doped ZTS crystals. Thermogravimetry detects weight loss of material as a function of temperature[3]. From TGA, different kinetic parameters such as activation energy, entropy, enthalpy and gibbs energy was deliberated.

Keywords: Gel growth; Zinc Thiourea sulfate (ZTS); Thermogravimetric Analysis (TGA), Broido method.

1. Introduction

Growth of perfect crystals of many materials and their studies are concern to many scientists. Crystals are important in device fabrication. Single crystals are important in many devices such as rectifiers, lasers, modulators, polarizers, computer chips, etc. Crystals have so many applications. So, for scientific and industrial development their growth procedure and their characteristics are significant. The popular and most common gel is silica gel, also called hydro gel or water gel. When powder of sodium meta silicate is mixed with aqueous solution, mono silicic acid is produced.

$$\underset{\text{Sodium meta silicate}}{Na_2SiO_3} + 3H_2O \rightarrow \underset{\text{Mono silicic acid}}{H_4SiO_4} + 2NaOH$$

This mono silicic acid can polymerized with release of water and procedure is repeated continuously and formed three dimensional networks of Si-O links as a hydrogel. Doping of the crystals is also important to get desired morphology and characteristic of crystals. The present work aims to understand growth of the doped crystals in the gel medium and influence on the thermal property of Zinc thioura sulphate (ZTS) crystals when doped with ferrous chloride, barium chloride and ammonium chloride. Thermo gravimetric analysis (TGA) observes the weight changes in the sample as a function of temperature. TGA analysis is used to find the composition of sample and to predict their thermal stability up to elevated temperature [4]. It is useful for evaluating kinetic parameters of various reactions and materials.

2. Materials and Methods

In the present work, crystals were grown by single diffusion gel growth technique. Gel growth is an intermediate between growth in solid and in solution. Sodium meta silicate, also called silica gel or SMS was used to form a gel medium. Particular density was obtained by pouring distilled water to the sodium meta silicate (SMS). This solution is called stock solution and can be conserved it for future use. When any mineral or organic acid mixed with the stock solution, gel formed. Irrespective of the process and structure, gelation behaviour depends on many factors such as density of gel, pH of gel, the solvent used and the temperature. It was shown [5] that during gelation process, hydoroxy ions are continuously being liberated and consequently, the gelation time is very sensitive to pH. To set precise pH, stock solution was acidifying by the dilute acetic acid with continuously stirring the solution.

AR grade Zinc Sulfate Heptahydrate and Thiourea were taken in 1:3 molar ratios in different beakers. After adjusting the density (1.05gm/cc) and pH, with the help of stirrer for with 48° temperature 3N Thiourea was prepared to avoid decomposition. This solution was poured in the main solution and stirred it again for 1 hour.

For ferrous chloride doped Zinc thiourea sulfate crystals, 10 ml of 1N of ferrous chloride with 1.05gm/cc density and 4.24 pH was prepared and stirred separately for 1 hours. This solution was mixed as a dopant in solution (in thiourea) and also stirred for 2 hours. Dopant mixed final solution (with thiourea and SMS solution) orange coloured solution was stirred for 2.30 hours at 550 rpm. The final solution was filtred 2-3 times and poured carefully in the test tubes. The gel setting time was found to be 18 days. After the gel set, 1N zinc sulfate heptahydrate was prepared in distilled water and poured it over the top of the set gel in the test tubes as a second reactant. For prevent evaporation, the test tubes ends were closed by cotton pads or paper caps.

For barium chloride doped ZTS crystals, 1N of barium chloride with 1.05gm/cc density and pH value of 4.31 was prepared and stirred for 1 hour and dopant mixed solution stirred for 2.30 hours. Final solution also stirred for 2 hours at 700 rpm. The gel setiing time 5 to 10 days. And crystal growth time after zinc sulphate heptahydrate was poured was 7 to 10 days. [6]

For ammonium chloride doped ZTS crystals, ammonium chloride with 1.05 gm/cc and pH value of 4.31 was prepared with 5N solution and stirred for 1 hour. While solution with dopant were stirred for 2 hours and final solution was stirred for 2 hours. Gel setting time was 13 days and crystal growth time after zinc sulphate heptahydrate was poured was 6 weeks.

Grown crystals were analysed for the thermo garavimetric analysis (TGA). TGA was carried out using Perkin Elmer Pyris-6 TGA thermal analyser. The smple continuously weighed as it heated at the rate of 10°C/min to elevated temperature. The sample under test was put in the open pan to be placed in furnace of TG analyser and adhere to automatic recording balance. When the temperature was increased in uniform constant rate, the weight loss can be recorded with time. The heating was carried out between the range of 25°C to 800°C. Broido method [7] was used to evaluate the kinetic parameters from the thermogram.

In TGA evaluation, the conversion of weight calculated as $Y = N/N_0 = (W_t\text{-}W_f) / (W_0\text{-}W_f)$

= fraction of the number of initial molecules not yet decomposed.

Where W_t = weight of active material at absolute temperature T.

W_0 = weight of the material taken initially.

W_f= weight of the material at the end of the reaction.

The pyrolysis being carried out isothermally, the reaction rate is given by

$$dY/dt = -kf(Y)$$

Where, f(Y)= differential expression of kinetic reaction model with function k which is specific rate constant, and n=1 in present case. Here k changes with temperature, according to the Arrhenius equation;

$$K = Ae^{-E/RT}$$

Where, A= pre exponential factor (Arrhenius constant) is accepted as independent of temperature, E = activation energy of degradation reaction with unit (kJ/mol), T= absolute temperature in 'K' and R= universal gas constant with value 8.314 J/mol.K. combine above two equation, the formula is written as

$$\frac{dT}{dt} = Af(Y)\, e^{-E/RT}$$

in degradation process, temperature of sample can change by constant heating rate 'β' (dT/dt) under controlled condition. The difference in degree of conversion of weight can be resolve as a function of temperature and determined by time of heating. So, rate of reaction can express as

$$\frac{dY}{dt} = \frac{dY}{dT}\cdot\frac{dT}{dt} = \beta\frac{dY}{dT}$$

So, the change in weight and temperature can mentioned as following equation

$$\frac{dY}{dT} = \frac{A}{\beta}\int_{Tc}^{Tp} e^{\frac{-E}{RT}}\, dT$$

Using the approximation, Broido rearrange the above equation and obtain following equation as

$$\ln\left[\ln\frac{1}{Y}\right] = \frac{-E}{RT} + \left[\frac{RAT_{max}^2}{E_a\beta}\right]a \qquad \text{or} \qquad \ln\ln(1/y) = E/(RT) + \text{constant}$$

Order of thermal degradation would take as first order in Broido's approximation and calculation done accordingly. After obtaining the energy of activation (Ea) from Broido's method the entropy of activation (ΔS) can be evaluated using following equation,

$$\Delta S = R\cdot\ln\left(\frac{Ah}{k_B T_s}\right)$$

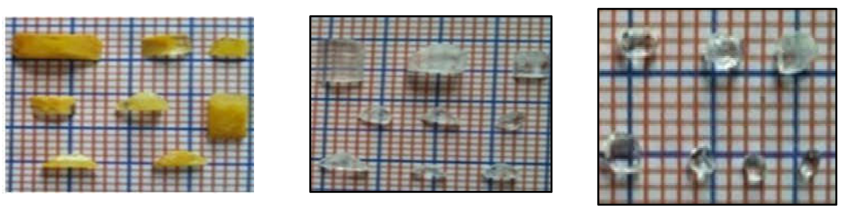
Here, h and k_B shows Planck's constant and Boltzmann constant respectively and Ts peak temperature. The enthalpy of activation (ΔH) and Gibbs energy (ΔG) can be determined using the below relationship of equation.

$$\Delta H = E - RT, \quad \Delta G = H - T\Delta S \qquad \text{or} \qquad E\,(eV) = slope * k / 1.6 \times 10-19$$

3. Results and Discussion

3.1 Growth

Ferrous chloride doped, barium chloride doped and ammonium chloride doped ZTS crystals were grown by gel technique. Ferrous chloride doped ZTS crystals has yellowish color, where as barium chloride doped ZTS and ammonium chloride doped ZTS crystals are transperent. The crystals of the different size and morphology is described in the figure 1 below:



(a) ferrous chloride doped ZTS crystals

(b) barium chloride doped ZTS crystals

(c) ammonium chloride doped ZTS crystals

Figure 1 Different morphology chloride doped ZTS crystals; (a) ferrous chloride doped ZTS crystals; (b) barium chloride doped ZTS crystals; (c) ammonium chloride doped ZTS crystals.

Table 1. Grown crystals normality, density, pH, gel setting time, crystal growth time.

Crystals	**Normality**	**Density gm/cc**	**pH**	**Gel setting time**	**Crystal growth time**
Ferrous Chloride doped ZTS	1N	1.05	4.24	18 days	1 week
Barium Chloride doped ZTS	1N	1.05	4.31	5-10 days	7-10 days
Ammonium Chloride doped ZTS	5N	1.05	4.31	13 days	6 weeks

3.2 TGA

Themogram of ferrous chloride doped ZTS, barium chloride doped ZTS and ammonium chloride doped ZTS are shown in the figure 2, 3 and 4 respectively. The kinetic parameters are also calculated as shown in table 2.

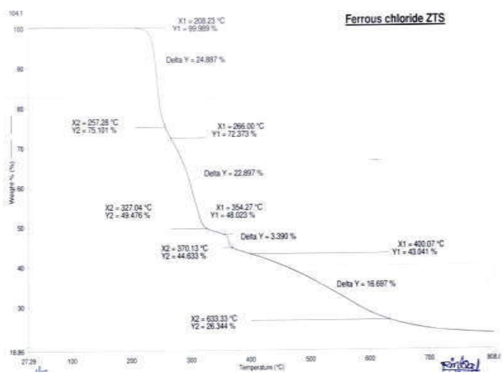


Figure 4 Thermogram of ferrous chloride doped ZTS crystals

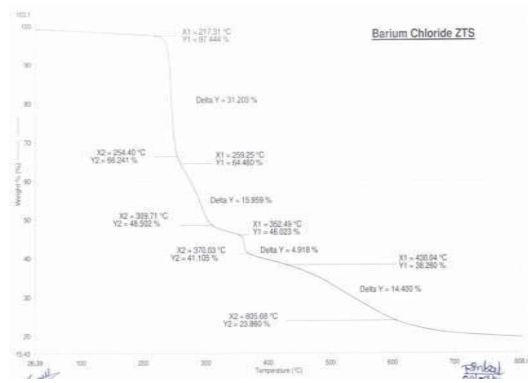


Figure 4 Thermogram of barium chloride doped ZTS crystals

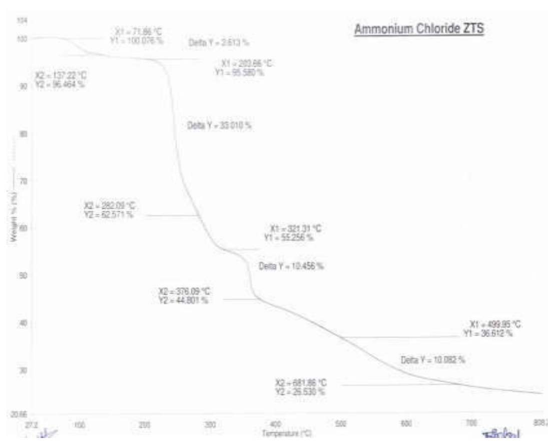


Figure 4 Thermogram of ammonium chloride doped ZTS crystals

The thermo gram of ferrous chloride doped ZTS, barium chloride doped ZTS and ammonium chloride doped ZTS crystal was studied in temperature region 25.000C to 800.000C, it shows four stage of decomposition. For ferrous chloride doped ZTS crystals, minimum weight loss is 3.390% at stage3 is more stable. Minimum weight loss for barium chloride doped ZTS crystals is 4.918% at stage 3 and weight loss for ammonium chloride doped ZTS crystals is 3.612% at stage 1 is more stable. Average mass loss of the ferrous, barium and ammonium chloride doped ZTS crystals are shown in table 2 below.

Table 2. Average mass loss of ferrous chloride, barium chloride and ammonium chloride doped ZTS crystals

	Crystals		
	Ferrous chloride doped ZTS	Barium chloride doped ZTS	Anium chloride doped ZTS
Mass loss %	16.968	16.620	14.290

From the table ammonium chloride has a less mass loss compared to ferrous chloride and barium chloride doped ZTS crystals. So, ammonium chloride doped ZTS crystals can withstand at high temperature and had a less mass loss i.e., more stable. Calculated kinetic parameters of doped crystals are shown in table 3 below.

Samples	Activation energy (J/mol)	Frequency factor (s^{-1})	-ΔS ($J.K^{-1}.mol^{-1}$)	ΔH (KJ/K)	ΔG (KJ)
Ferrous chloride doped ZTS	170.554	37.5495	450.525	165.3561	307.1853
Barium chloride doped ZTS	118.3567	25.3627	226.3970	124.1271	265.9374
Ammonium chloride doped ZTS	72.4127	17.9427	227.8797	67.4659	204.3934

From the table conclude that the greater the activation energy, the lower the rate of reaction. It means that ferrous chloride doped ZTS crystals has low rate of reaction. Negative entropy means something has less disorder, or more order. Barium chloride and ammonium chloride doped ZTS crystals are more ordered . Positive enthalpy suggests that there is a endothermic realction occurred. Positive gibbs energy suggests the reaction will occure non-sponatneously.

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