Study Of Thermal Properties Of ZTS Crystal Grown By Gel Technique

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***Abstract:** Zinc Tris-thiourea Sulfate (ZTS) is a Semi Organic Nonlinear Optical (NLO) material which finds applications in the area of laser technology, optical communication, data storage technology, and optical computing etc. The author has successfully grown ZTS crystal by gel method. Gel technique has been adopted at ambient temperature to attain better result. The grown crystals were transparent and colourless. The crystal size has been obtained the range about 5mm X 3mm X 2mm. Thermal study of ZTS crystal from Thermo-Gravimetric Analysis (TGA) and calculate activation energy and other Thermal parameters.*

***Keywords:** ZTS Crystal, TGA Analysis, Activation Energy*

I. INTRODUCTION

Zinc Tris-thiourea Sulfate (ZTS) is a Semi Organic Nonlinear Optical (NLO) material which finds applications in the area of laser technology, optical communication, data storage technology, and optical computing, etc. Zinc Tris-thiourea Sulfate (ZTS), $Zn[CS(NH_2)_2]_3SO_4$ is a semi-organic material for academic research and industry. Usually, the ZTS crystal grown by Slow Evaporation Solution Method, Aqueous Solution by Slow Cooling Method, Free Evaporation Method and rarely Sankaranarayanan-Ramasamy (SR) Method was used to grow ZTS crystal. Gel technique has been adopted at ambient temperature to attain better result. The gel technique for the ZTS crystal grows by I.B.Patel et al. The crystal structure of ZTS for the first time was determined by single crystal X-ray determination method. It is a well characterized material of non-centrosymmetric orthorhombic crystal system with lattice parameters a = 11.126 Å, b = 7.773 Å, c = 15.491 Å and space group $Pca2_1$ (Point group mm2). It exhibits a low angular sensitivity and the SHG phenomenon. Compared to potassium dihydrogen phosphate the SHG efficiency was found to be ~ 2 times for 1064 nm fundamental wavelength. From Raman and Fourier Transform Infrared (FTIR) spectroscopy the extensive vibrational studies have been carried out on ZTS. ZTS crystals are found to possess high laser damage threshold and wide optical transparency. High damage threshold and wide transparency make it a better alternative for KDP crystals in frequency – doubling and laser fusion. The Curie temperature (FE-PE phase transition) of ZTS is T_c = 323 K. Venkatraman et al. have determined the melting point of ZTS accurately by direct observation method at 234°C. Several authors have reported the growth rate and influence of solution pH on the morphology of ZTS crystals.

II. EXPERIMENT

GEL GROWTH

For present study, the authors have successfully grown ZTS crystals by Gel technique at ambient temperature. For experiment silica gel or Sodium Meta Silicate is used to

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prepare gel. Sodium Meta Silicate (SMS) solution was prepared by Distilled Water. The solution was filtered by the filter paper about 4 to 5 times. For different pH, the Acitic Acid was poured in to the solution. Pour different test tubes for different pH. To avoid porous gel and decomposition, 3N Thiourea using stirrer at 42^o C temperature were prepared. These thiourea as a feed solution was poured in the different pH test tubes which is filled with the SMS solution. Zinc Sulfate Heptahydrate (AR Grade) and Thiourea (AR Grade) were taken in 1:3 ratios. Then, gel solution was allowed to set at ambient temperature. After completing reaction between Zinc Sulphate Heptahydrate and Thiourea, by following reaction ZTS crystal was synthesised within 4-6 weeks:

$$ZnSO_4 \cdot 7\,H_2O + 3\,CS(NH_2)_2 \longrightarrow Zn[CS(NH_2)_2]_3SO_4 + 7H_2O$$

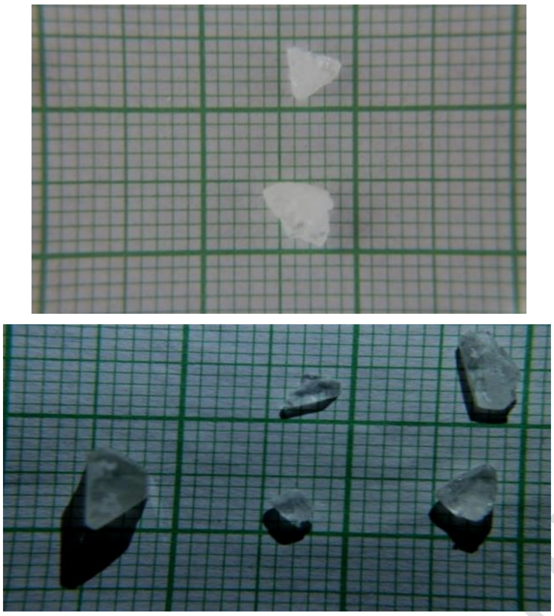

Figure 1: ZTS Crystal grown by gel method

THERMAL ANALYSIS

The weight loss and thermal stability of sample were analysed by Perkin Elmer Pyris-6 TGA analyser at heating rate of 10^o C/min. for temperature range 30^oC to 900^oC. The recorded thermogram is shown in fig.2. It reveals that there were three stages of decomposition occurred i.e., the first stage weight loss was about 50.2% take place in the region 202.73^oC to 310.00^oC, second stage weight loss was about 15.592% in the region 310.91^oC to 364.55^oC and third stage weight loss was about 18.592% in the region 440.65^o C to 747. 20^oC.The activation energy and frequency factor using Broido relation was also carried out. Graph was shown in fig.3, 4, 5.

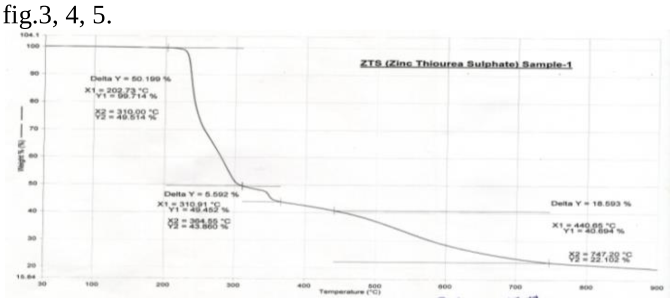

Figure 2: Thermogram of the pure ZTS crystal

ACTIVATION ENERGY

Broido relation was used to calculate the activation energy "E" and the frequency factor "z". When a pure solid substance is heated in vacuum, it undergoes pyrolysis in which at least some of the pyrolysis products are volatile. W_t, the weight at any time t, is related to the fraction of the number of initial molecules not yet decomposed, y, by the equation,

$y = \frac{N}{N_0} = \frac{W_t - W_\infty}{W_0 - W_\infty}$ = fraction of the number of initial molecules not yet decomposed.

Where W_t = Weight of active material at absolute temperature, W_0 = Weight of the material taken initial, W_∞ = Weight of active material at the end of the reaction. According to Arrhenius equation, the activation energy is calculated by

$$ln\,ln\frac{1}{y} = \frac{E}{RT} + \text{constant} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Thus the slope of the plot of lnln(1/y) ➔ 1/T (fig. 3,4 and 5) yields the required energy of activation (see table:1). The plot gives a good linear fit for n=1.

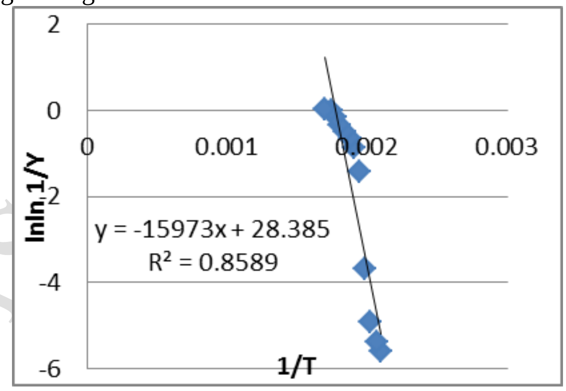

Figure 3

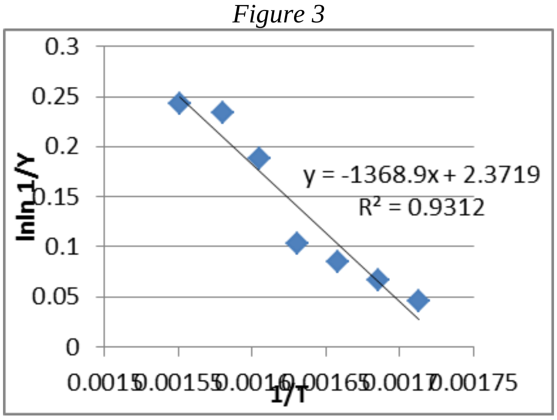

Figure 4

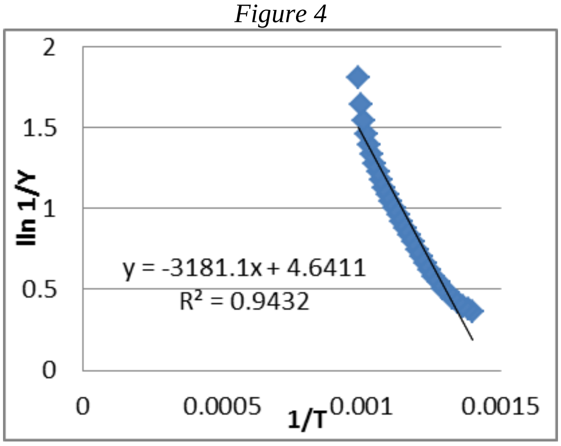

Figure 5

Fig. Broido relation (fig.3. stage1: temp. 202.73-310°C, fig.4. stage2: 310.91-364.55°C, fig.5. stage3:440.65-747.2°C)

ENTROPY, ENTHALPY AND GIBB'S ENERGY

Entropy is defined as the energy that is distributed or dispersed among the various motions of molecules of the crysatal. The value of entropy S were also obtained from the activation energy "E" and frequency factor "z" by using the equation:

$$Z = \frac{kTm}{h} . \exp \frac{S}{R} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where k = Boltzmann's constant = 1.38 x 10^{-23} J(^{0}K^{-1}), h = Plank's constant = 6.626 x 10-34 J.S

Enthalpy can be defined as the heat that is evolved or absorbed in the reaction. The value of Enthalpy H was calculated by the equation

$$H = E_a - RT \qquad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where Ea = Energy of activation, T = Temperature in ^{0}K and R= Gas Constant = 8.31432 in J (K^{-1} mol^{-1})

Gibbs energy was calculated by using entropy and enthalpy by the equation

$$G = H - TS \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4)$$

III. RESULT AND CONCLUSION

Successfully grown ZTS crystal by gel method at ambient temperature. The quality of grown ZTS crystal was good and transparent. The crystal average size has been obtained the range about 5mm X 3mm X 2mm.From the TGA thermogram and used broido relation calculates activation energy, frequency factor, Gibbs energy, Entropy, Enthalpy.

Stage	Temp Range in°C	Activation Energy in KJ	Frequency factor in min^{-1}	Gibbs energy in KJ/mol	Entropy in J/Kmol	Enthalpy in joule
1	202.73-310	-1.4237 x 10^{-23}	28.38	1.0579 x 10^5	-208.60	-4391.87
2	310.91-364.55	0.1166 x 10^{-23}	2.371	1.3176 x 10^5	-223.48	-5091.29
3	440.65-747.2	1.0780 x 10^{-23}	4.641	1.9337 x 10^5	-232.38	-7175.43

Table 1

CONCLUSION

Good optical quality pure ZTS single crystals have been successfully grown by gel technique. A convenient size of 5mm X 3mm X 2mm was harvested. It was observed that the weight loss at stage 2 which is at the temperature range of about 310.91°C to 364.55°C is 15.592% was more stable. From TGA analysis thermal stability of the grown crystal was observed up to 202.73°C. start the decomposition further from 202.73°C.The activation energy (E) of the pure ZTS crystal for stage 1 is -1.4237x10^{-23} in KJ and the frequency factor is 28.38 min^{-1}, for stage 2 activation energy (E) is 0.1166 x 10^{-23} in KJ and frequency factor is 2.371 min^{-1} and for stage 3 activation energy (E) is 1.0780 x 10^{-23} in KJ and frequency factor is 4.641 min^{-1}.

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