*Section A -Research paper*

# Investigation of Thermodynamical parameters of $Zn_xMg_{(1-x)}TS$ Single Crystals

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**Abstract:** A wide variety of novel inorganic, organic and semi organic non-linear optical materials are being developed in recent years. For the transmission of data, in many devices photons are used instead of electrons and the development in nonlinear optical crystals aids this application. In this aspect, in the present work tailor-made semi-organic NLO crystals of $Zn_xMg_{(1-x)}TS$ were grown by slow evaporation techniques for various values of x (x = 0 to 1). The density of the grown crystals was determined by conventional flotation technique and composition was estimated from the measured density. The thermodynamical parameters like melting point, thermal stability, thermal activation energy, frequency factor, entropy, enthalpy and Gibb's free energy were determined by using Broido Method, Coats and Redfern Method and Horowitz and Metzger Method from the TG/DSC curves recorded in the temperature range 30 to 1010ºC. The thermal activation energy, frequency factor, entropy and enthalpy were determined to vary non-linearly with bulk composition, and also observed that the thermodynamical parameters obey Horowitz and Metzger method.

**Key Words:** ZMTS mixed crystals, Density, Thermal activation energy, Entropy, Enthalpy, Gibb's free energy.

## 1. Introduction

Semi-organic materials gains prominence in the non-linear optics for real time applications[1]. The organic ligand and inorganic host was subjected to ionic bonding, results in novel materials with good optical nonlinear property [2]. The TG/DTA was found to be a proficient one for the estimation of thermal behaviour and also describes the decomposition levels of the materials [3]. In earlier study N. Bhuvaneswari Arvind et al [4] reported that Tris-Thiourea Magnesium Zinc Sulphate crystal was thermally stable up to 248.75ºC. A. Darlin Mary et al [5] studied the thermogravimetric analysis of ZTS and MTS mixed crystals. The magnesium when mixed with ZTS, the melting point of ZTS was found to be increased and then decreased slightly. The melting point of MTS was found to be 181.40°C. The thermal stability of ZTS was found to decrease with the addition of different concentration of magnesium and observed a no phase transition till the materials melt. V.S. Kumar and R.S.

Sundararajan [6] reported that Tris-Thiourea Zinc Magnesium Sulphate crystal was thermally stable up to 265ºC. I.B.Patel [7] observed that the thermal stability of ZTS was 202.73$^0$C. Using the Broido relation they calculate the activation energy, frequency factor, entropy, enthalpy and Gibbs energy. The activation energy, frequency factor for the temperature range 202.73$^0$ -310$^0$C was found to be -1.4237 x10$^{-23}$ kJ and 28.38 min$^{-1}$ respectively. G.Pasupathi and P.Philominathan [8] have reported that the melting point of MTS was 153$^0$C.S.Gunasekaran et al [9] have studied the thermal properties of UMTS, BMTS and TMTS. They reported that the melting point of UMTS, BMTS and TMTS are 232$^0$C, 231$^0$C and 236$^0$C respectively. S.Alfaify et al [10] added $Mg^{2+}$ and M.Selvapandiyan et al [11] added $MgSO_4$ to ZTS. They all reported that thermal stability and melting point of doped ZTS was greater than that of pure ZTS, and also pointed out that increase in thermal stability and melting point may be due to the incorporation of dopant atom.

In the present research work mixed crystals of $Zn_xMg_{(1-x)}TS$ were grown by slow evaporation technique. The density of the crystals was determined by conventional flotation technique and bulk composition was also determined from the density values. Thermodynamical parameters were evaluated from TG/DSC curves using Broido method, Coats and Redfern method and Horowitz and Metzger method. Section 2 describes the experimental details and the results are highlighted in section 3

## 2. **Experimental Details**

The ZMTS salts were synthesized by the stiochiometric mixing of Zinc Sulphate heptahydrate and Magnesium Sulphate heptahydrate with Thiourea in the molar ratio1:3.The compounds are dissolved in deionized water, followed by stirring using a magnetic stirrer and finally the mixture was heated at 50℃.

The chemical reaction involved in this process is as follows

$$Zn_xMg_{(1-x)}SO_4 .7H_2O + 3CS(NH_2)_2 \rightarrow Zn_xMg_{(1-x)} [(CS(NH_2)_2)_3] SO_4 \quad (1)$$

where, x = 0 to 1 in steps of 0.1

The slow evaporation technique was employed in this research work for the growing of Single crystals of ZMTS. Totally eleven crystals were grown (9 mixed and 2 end member crystals).The density of the crystals were determined by conventional flotation technique using bromoform (2.894 g/cc) and ethanol (0.78 g/cc) as higher and lower density liquids respectively. The bulk compositions of the mixed crystals were estimated from the density of the grown crystals. The crystalline properties of a sample can be estimated from its melting behavior via thermal analysis. Thermal analysis gains prominence industrial sector, it depicts the change in the physical property of material with respect to temperature [12, 13 and 14]. The thermal characterization of the grown crystals was studied using TG/DSC curves recorded in the temperature range 30 to 1010ºC using STA 449F3 Jupiter Instrument at NETZSCH Technologies India Pvt. Ltd, Chennai. The thermodynamical parameters like melting point, thermal stability, thermal activation energy, frequency factor, entropy, enthalpy and Gibb's free energy were determined from the TG/DSC curves.

Thermal activation energy is the minimum amount of energy needed to initiate thermal reaction or it can also be defined as the energy that is required in a chemical system for the chemical reaction to take place. There is much literature works describing the different techniques for the estimation of thermal activation energy [15-22]. In this research work, the thermal activation energy and kinetic parameters were estimated by using Broido method, Coats and Redfern method and Horowitz and Metzger method.

In the Broido model the activation energy at each stage of decomposition ($E_a$) and the frequency factor (A) was evaluated from the Arrhenius relation

$$\ln\ln\left(\frac{1}{y}\right)=\frac{-E_a}{RT}+\text{ Constant} \qquad (2)$$

$$\text{Where } y=\frac{w_t-w_\infty}{w_o-w_\infty}$$

y is the fraction of the number of molecules not yet decomposed, $w_t$ is the weight of the material, $w_o$ is the initial weight of the material and $w\infty$ is the weight of the residue.

To determine the activation energy, plot a curve between $\ln(\ln\left(\frac{1}{y}\right))$ versus 1/T. From the slope of line of best fit, the activation energy ($E_a$) was determined and the intercept gives the frequency factor (A).

The expression for the estimation of activation was put forward by Coats and Redfern, the order of the reaction is a vital parameter.

For first-order reaction when n = 1 the equation is as follows

$$\log_{10}\left(\frac{-\log(1-\alpha)}{T^2}\right)=\left[\log_{10}\left\{\left(\frac{AR}{\alpha E_a}\right)\left(1-\frac{2RT}{E_a}\right)\right\}-\left(\frac{E_a}{2.303RT}\right)\right] \qquad (3)$$

$$\text{Where } \alpha=\frac{w_o-w_t}{w_o-w_f}$$

$w_o$ is the initial weight, $w_t$ is the weight at time and $w_f$ is the finial weight of the material .A plot of $\log_{10}$[-log (1-α)/$T^2$]verses 1/T will result in a straight line having slope ($E_a$/2.303R) from which activation energy ($E_a$) was calculated and the intercept gives the frequency factor (A).

The activation energy was estimated using the integral equation of Horowitz and Metzger. The equation used for the estimation of energy of activation ($E_a$) is as follows

$$\ln\ln\left(\frac{w_o}{w_t}\right)=\frac{\theta E_a}{RT^2} \qquad (4)$$

where, θ=(T-$T_s$),the difference between the maximum temperature and the temperature at particular weight loss, $w_o$ is the initial weight, $w_t$ is the weight at any time t, $T_s$ is the maximum temperature and T is the temperature at particular weight loss. A plot of lnln ($w_o$)/ ($w_t$) versus θ gives a straight line. From the slope the activation energy can be calculated.

Entropy is the energy that is distributed or dispersed among the various motions of molecules of the crystal. The entropy (ΔS) can be calculated using the relation [23].

$$\Delta S = 2.303 \times R \times \log_{10}\left[\frac{Ah}{kT}\right] \quad (5)$$

where, R is the universal gas constant, A is the frequency factor, h is the Planck's constant, k is the Boltzmann constant and T is the melting point.

Enthalpy is the heat that evolved or absorbed in the reaction. The Enthalpy (ΔH) was calculated using the equation [24]

$$\Delta H = E_a - RT \quad (6)$$

where, $E_a$ is the Energy of activation.

Gibb's free energy is associated with a chemical reaction that can be used to do work. It can be determined from entropy and enthalpy by using the relation

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

## 3. Results and Discussion

The photograph of all the grown crystals are shown in figure1. The morphology of the crystals grown in the present study were diamond shape of 1mm thickness and they are opaque and white in colour.

Top : ZTS, MTS, $Zn_{0.1}Mg_{0.9}TS$, $Zn_{0.2}Mg_{0.8}TS$

Middle : $Zn_{0.3}Mg_{0.7}TS$, $Zn_{0.4}Mg_{0.6}TS$, $Zn_{0.5}Mg_{0.5}TS$, $Zn_{0.6}Mg_{0.4}TS$

Bottom : $Zn_{0.7}Mg_{0.3}TS$, $Zn_{0.8}Mg_{0.2}TS$, $Zn_{0.9}Mg_{0.1}TS$

**Fig. 1: Photograph of all the grown crystals**

The measured density and the bulk composition estimated from the density values are given in Table.1.

**Table 1: Density and Estimated bulk composition of all the grown crystals**

| Sample | Density (g/cc) | Estimated bulk Composition |
|---|---|---|
| ZTS | 1.7317 [1.942] [26] | - |
| MTS | 1.6038 [1.6087] [27] | - |
| $Zn_{0.1}Mg_{0.9}TS$ | 1.6149 | $Zn_{0.0868}Mg_{0.9132}TS$ |
| $Zn_{0.2}Mg_{0.8}TS$ | 1.6318 | $Zn_{0.2189}Mg_{0.7811}TS$ |
| $Zn_{0.3}Mg_{0.7}TS$ | 1.6401 | $Zn_{0.2838}Mg_{0.7162}TS$ |
| $Zn_{0.4}Mg_{0.6}TS$ | 1.6520 | $Zn_{0.3769}Mg_{0.6231}TS$ |
| $Zn_{0.5}Mg_{0.5}TS$ | 1.6654 | $Zn_{0.4816}Mg_{0.5184}TS$ |

| | | |
|---|---|---|
| $Zn_{0.6}Mg_{0.4}TS$ | 1.6829 | $Zn_{0.6185}Mg_{0.3815}TS$ |
| $Zn_{0.7}Mg_{0.3}TS$ | 1.6972 | $Zn_{0.7303}Mg_{0.2697}TS$ |
| $Zn_{0.8}Mg_{0.2}TS$ | 1.7120 | $Zn_{0.8460}Mg_{0.1540}TS$ |
| $Zn_{0.9}Mg_{0.1}TS$ | 1.7226 | $Zn_{0.9289}Mg_{0.0711}TS$ |

The density value reported earlier for ZTS and MTS single crystal are given in square brackets. It is found that the density of the mixed crystals shows linear variation with the composition of zinc. As the composition of the zinc increases the density of the mixed crystals also found to be increased. The composition estimated for the mixed crystals from the density values well agreed with the actual composition taken.

**Inference from the TG/DSC curve:** TG/DSC curve for the mixed crystal $Zn_{0.5}Mg_{0.5}TS$ crystal is shown in figure 2 for illustration. The crystals grown in the present research study was found to be thermally stable from 180°C to 195°C. The grown crystals do not contain the water molecule because there is no weight loss around 100ºC.

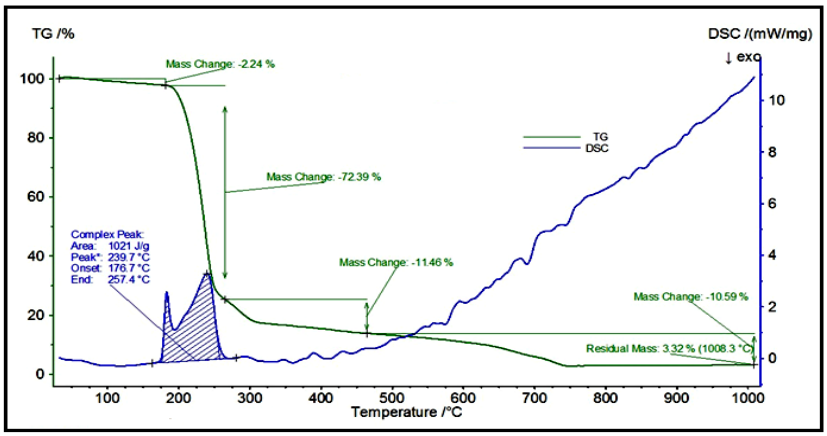


**Fig. 2: TG/DSC curve of $Zn_{0.5}Mg_{0.5}TS$ crystal**

The graph drawn between lnln $(\frac{1}{y})$ Vs 1/T for the mixed crystal $Zn_{0.7}Mg_{0.3}TS$ is shown in the figure3.

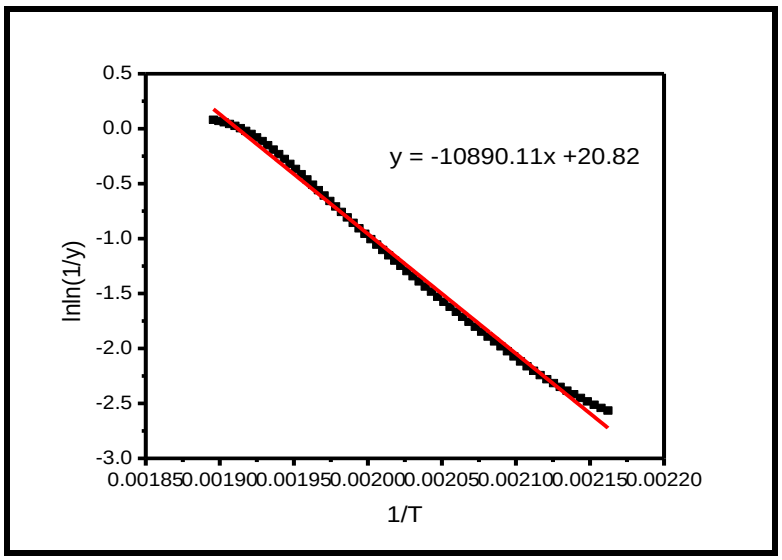


**Fig. 3: Variation of lnln(1/y) with 1/T for $Zn_{0.7}Mg_{0.3}TS$ crystal**

The curve drawn between $\log_{10}$ [-log (1-α)/$T^2$] verses 1/T for the mixed crystal $Zn_{0.3}Mg_{0.7}TS$ is shown in the figure 4.

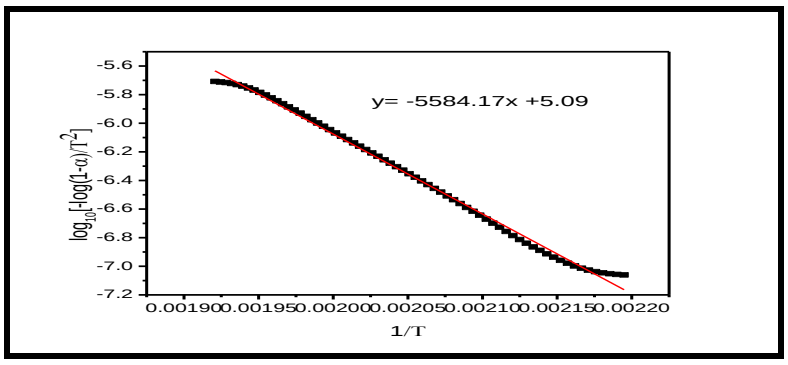


**Fig. 4: Variation of $\log_{10}$ [-log(1-α)/$T^2$) with 1/T for $Zn_{0.3}Mg_{0.7}TS$ crystal**

The graph drawn between lnln($w_o$)/ ($w_t$) versus θ for the mixed crystal $Zn_{0.8}Mg_{0.2}TS$ is shown in the figure 5 for illustration.

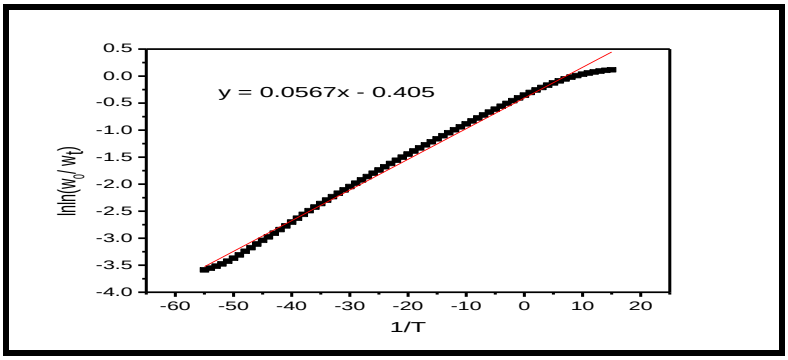


**Fig. 5: Variation of lnln($W_0$/$W_t$) 1/T for $Zn_{0.8}Mg_{0.2}TS$ crystal**

The results in graph reveal that, transitions follow a straight line and obey the Arrhenius behaviour. Negative slope was observed in the transitions on the heating scan due to the heat absorption. The endothermic peak shift towards the lower range temperature values with respect to the decrease in ramp rate [25]. In the case of Horowitz and Metzger method positive slope is obtained. The melting point of the ZTS and MTS crystals agreed with the values reported earlier. The melting point of the mixed crystals shows non-linear variation with bulk composition. The variation of activation energy with composition for the three models is shown in figure 6.

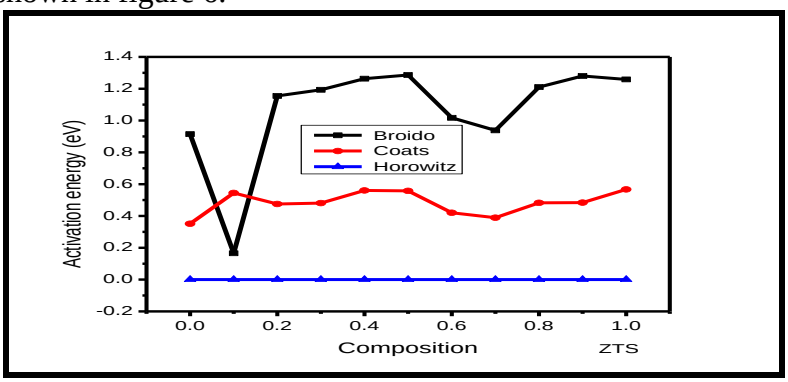


**Fig. 6: Variation of Activation energy (eV) with composition for the three methods**

The melting point and thermal stability are given in the Table2.

**Table 2: Melting point and Thermal Stability for all the grown crystals**

| Sample | Melting Point (K) | Thermal stability (°C) |
|---|---|---|
| ZTS | 495.3 [504][28] | 191.66 |
| MTS | 508.5 [454.40][5] | 189.15 |
| $Zn_{0.1}Mg_{0.9}TS$ | 531.7 | 193.31 |
| $Zn_{0.2}Mg_{0.8}TS$ | 526.9 | 189.15 |
| $Zn_{0.3}Mg_{0.7}TS$ | 509.4 | 185.00 |
| $Zn_{0.4}Mg_{0.6}TS$ | 512.3 | 185.00 |
| $Zn_{0.5}Mg_{0.5}TS$ | 512.7 | 189.15 |
| $Zn_{0.6}Mg_{0.4}TS$ | 515.1 | 189.15 |
| $Zn_{0.7}Mg_{0.3}TS$ | 510.9 | 181.09 |
| $Zn_{0.8}Mg_{0.2}TS$ | 515.1 | 185.00 |
| $Zn_{0.9}Mg_{0.1}TS$ | 509.3 | 181.19 |

The activation energy determined is low and it also varies non-linearly with bulk composition. The low activation energy indicates the autocatalytic effect of the metal ion on the thermal decomposition of the crystal [29]. The variation of entropy and frequency factor with composition for the three models is shown in figures 7 and 8 respectively.

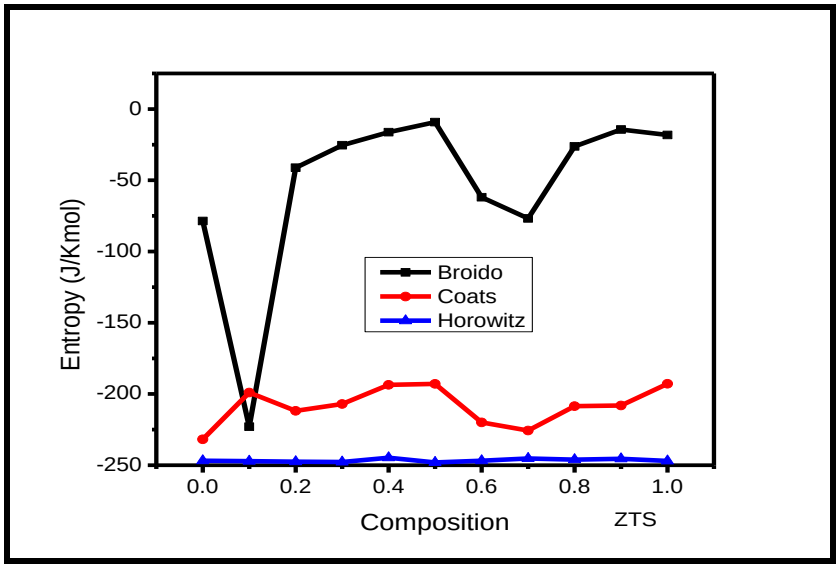


**Fig.7: Variation of Entropy (J/K mol) with composition for the three methods**

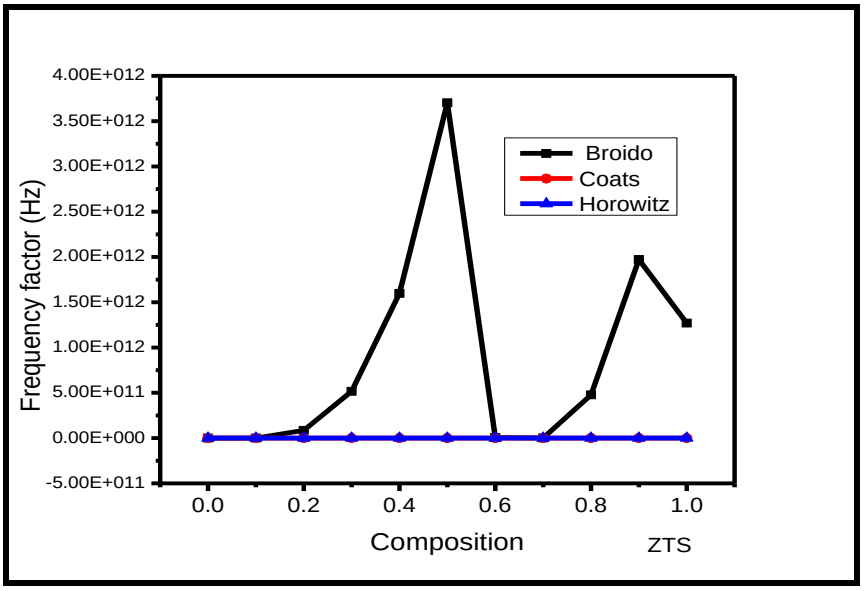


**Fig. 8: Variation of Frequency factor (Hz) wit composition for the three methods**

The entropy of all the mixed crystals show a non-linear variation with bulk composition and the value is negative. The activated complex was found to be more ordered, since the entropy value is negative. The high value of A indicates the fast nature of reaction. The polarization of bonds and fast nature of reaction accounts for the ordered nature of the activated complex [23].

The variation of enthalpy with composition for the three models is shown in figure 9.

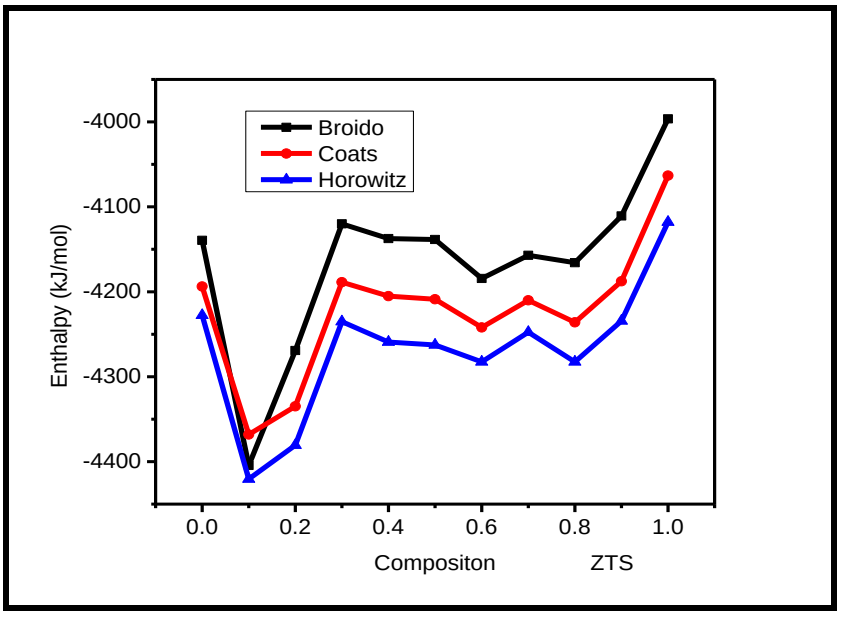


**Fig. 9: Variation of Enthalpy (kJ/mol) with composition for the three methods**

The enthalpy of reaction determined for the mixed crystals are negative and almost same. The negative sign indicates that the reaction is exothermic. The variation of Gibb's free energy with composition for the three models is shown in figure10 respectively.

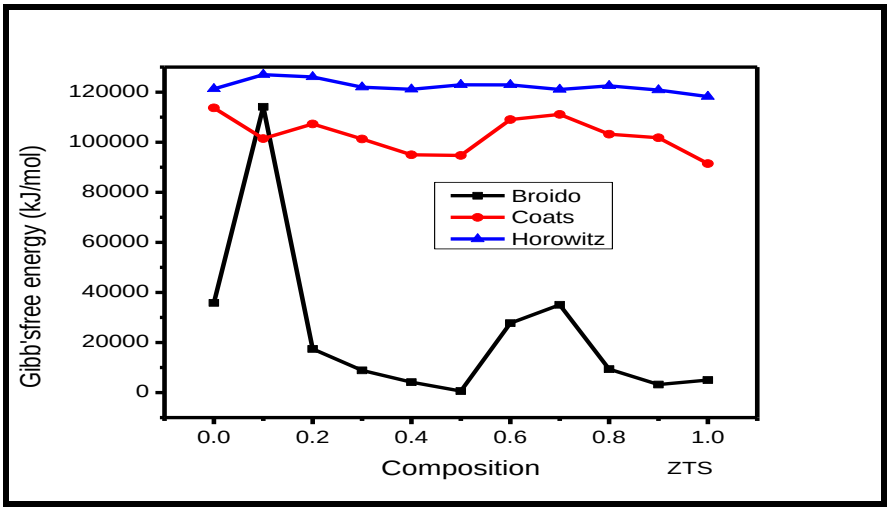


**Fig. 10: Variation of Gibb's free energy (kJ/mol) with composition for the three methods**

Gibbs energy determines the useful work delivered by a system and is a vital characteristic of a system. It determines, whether a state change is spontaneous or not. The ΔG value may be positive or negative and it is an indication of nature of the reaction; spontaneous or non-spontaneous. The negative value of ΔG represents the spontaneous nature of the reaction and positive value of ΔG represents the non-spontaneous nature of the reaction [30].Gibb's free energy determined in the present investigation is almost constant for all the mixed crystals using the Coats and Horowitz methods. The positive value of Gibb's energy shows that the reaction is non-spontaneous towards the products and spontaneous towards the reactants. Thermodynamical parameters like thermal activation energy, frequency factor, entropy and enthalpy determined vary non-linearly with bulk composition. From the figures 6, 7, 8 and10 the parameter varies linearly with composition determined from the Horowitz and Metzger method when compared to the other two methods. So we concluded that the Horowitz and Metzger method is suitable for this current system.

## 4. Conclusion

Thermodynamic properties of $Zn_xMg_{(1-x)}TS$ Single Crystals was investigated in this research work. The activation energy was determined by three methods; Broido, Coats and Redfern and Horowitz and Metzger methods. The activation energy varies non-linearly with bulk composition. The entropy of all the mixed crystals shows a non-linear variation with bulk composition and the value is negative. The enthalpy change is observed to be negative. The negative sign indicates that the reaction is exothermic. The positive value of Gibb's energy shows that the reaction is non-spontaneous towards the products and spontaneous towards the reactants. The Horowitz and Metzger method was found to be proficient in the estimation of activation energy.

## References

1. Fleck M, Becker P, Bayarjargal L, Ochrombel R, Bohaty L. 2008, "Crystal growth, crystal structure and physical properties of polar orthorhombic tris(glycine) zinc chloride", Cryst.Res.Technol. Vol. 43, pp.127-134.
2. Moitra S, Kar T. 2010, "Growth and characterization of L-valine -a nonlinear optical

crystal", Cryst.Res.Technol., Vol. 45, pp.70-74.

3. Sethu Gunasekaran, Padmapriya Venkatesan, Govindarajulu Anand and Subramanian Kumaresan 2012, "Thermal Properties of Pure and Doped BTMC and BTZS Single Crystals", International Journal of Chem Tech Research, Vol. 4, pp.1072-1076.
4. Bhuvaneswari Arvind, N, Baskar, K and Dhanasekaran. R. 2015, "Growth and Characaterization of Tris Thiourea Magnesium Zinc Sulphate single crystals" Optik, Vol. 126, pp. 3731-3736.
5. Darlin Mary, A, Jayakumari, K and Mahadevan, CK. 2013, "Growth and Characterization of Zinc- Magnesium Tris (Thiourea) Sulphate (ZMTS) Single Crystals", International Journal of Engineering Research and Applications, Vol.3, pp. 1183-1197.
6. Kumar, VS. and Sundarajan, RS. 2019, "Synthesis, growth and characterization of tris thiourea zinc magnesium sulphate single crystals", 7th National conference Hierarchically structured Materials (NCHSM-2019) AIP conference Proceedings 2117, 020023, https://doi.org/10.1063/1.5 114603.
7. Patel, IB, Dhruvi K.Vaghela, Kiran T.Rathod and Vanish Tandel 2017, 'Study OfThermal properties of ZTS Crystal Gown by Gel Technique', International Journal of Innovative Research and Advance Studies, Vol. 4, pp. 210-212.
8. Pasupathi, G and Philominathan, P 2009, 'Crystal Growth, Thermal, Optical and Microhardness studies of Tris (Thiourea) Magnesium Sulphate: A Semi-organic NLO Matetial', Modern Physics Letters B, Vol. 23, pp. 3035-30438.
9. Gunasekaran, S, Anand, G, Kumaresan,S and Kalainathan,S 2011, 'Mechanical, dielectric and thermal analysis of semi-organic NLO materials',Pelagia Research Library, Advances in Applied Science Research, Vol. 2,pp. 550-557.
10. Alfaify, S, Mohd.Shkir, Ganesh,V, Mohd. Anis and Yahi, IS 2018, 'A comprehensive investigation on core optoelectronic and laser properties of ZTS single crystals: an effect of $Mg^{2+}$ doping', Applied Physics B, Vol. 96, pp.1-12.
11. Selvapandiyan, M, Arumugam, J, Sundaramoorthi, P and Sudhakar, S 2013, 'Influence of $MgSO_4$ doping on the properties of Zinc tris-thiourea sulphate (ZTS) single crystals', Journal of Alloys and Compounds, Vol .580, pp. 270-275.
12. Maria Foldvari 2011, "Hand book of Thermogravimetric system of minerals and its use in geological practice", Geological Institute of Hungary, Budapest.
13. Wesley William Wendlandt 1986, "Thermal Analysis", 3rd Edition, Wiley-Interscience, New York.
14. Michael.E.Brown 1988, "Introduction to Thermal Analysis: Techniques and Applications", Chapman and Hall, New York.
15. Freeman, E.S and Carroll, B.J. 1958, "The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate", The Journal of Physical Chemistry Vol. 62(4), pp. 394- 397.
16. Horowitz, H and Metzger, G. 1963. "A new analysis of thermogravimetric traces", Analytical Chemistry, Vol. 35, pp. 1464-1468.
17. Coats, A.W and Redfern J.P. 1964, "Kinetic parameters from thermogravimetric data",Nature 201, pp.68-69.
18. Broido, A. 1969, "A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data", Journal of Polymer Science: Part A-2 (7), pp.1761-1773.
19. Sharp, J.H and Wentworth, S.A.1969,"Kinetic analysis of thermogravimetric data", Analytical Chemistry, Vol. 41(14), pp. 2060-2062.

20. Cao, M.Y and Wunderlich, B. 1985, "Phase transitions in mesophase macromolecules.V.Transitions in poly(oxy-1,4-phenylene carbonyl-co-oxy-2,6-naphthaloyl", Journal of Polymer Science , Vol. 23(3), pp. 521-535.
21. Li, X.G. Huang, M.R. Guan, G.H and Sun, T. 1998, "Kinetics of thermal degradation of thermotropic poly(P-oxybenzoate-coethyleneterephthalate) by single heating rate Methods" Polymer International, Vol. 46(4), pp. 289-297.
22. Chang, W.L. 1994,"Decomposition behaviour of polyurethanes via mathematical Simulation" Journal of Applied Polymer Science, Vol. 53(13), pp. 1759-1769.
23. Gayathri, K, Krishnan, P, Rajkumar, PR and Anbalagan, G.2014, "Growth, optical, thermal and mechanical characterization of an organic crystal: Brucinium 5-sulfosalicylate trihydrate", Bulletin of Materials Science, Vol. 37, pp. 1589-1595.
24. Yakuphanoglu, F, Gorgulu, AO and Cukurovali. A. 2004, "An organic semiconductor and conduction mechanism: N-[5-methyl-1,3,4-tiyodiazole-2-yl] ditiyocarbamate compound", Physica B, Vol. 353, pp. 223-229.
25. Dipti Sharma, John C. MacDonald and Germano S. Iannacchione 2006, "Thermodynamics of activated phase transitions of 8CB: DSC and MC Calorimetry", The Journal of Physics Chemistry B, Vol. 110, pp. 16679-16684.
26. Praveen, VN, Vijayan, N and Mahadevan, CK. 2012, "Dielectric measurements on urea added ZTS single crystals", Optik, Vol. 123, pp. 1617-1622.
27. Jeyalekshimi, M, Freeda, TH and Neelakanda Pillai, N. 2018, "Growth and Structural properties of MTS single crystal doped with $ZnSO_4$", International Journal of Science, Engineering and Management, Vol. 3, pp. 518-521.
28. Krishnan, C, Selvarajan, P, Freeda, TH and Mahadevan, CK. 2009, "Growth and Characterization of pure and Potassium Iodide-doped Zinc Tris-Thiourea Sulphate (ZTS) single crystals", Physica B, Vol. 404, pp. 289-294.
29. Patel. KR, Dhara Patel and Patel, VD. 2014, "Characterization, Activation energy and thermodynamic parameter of crystals synthesized from solvent evaporation method", International journal of Researches in Biosciences and Agriculture Technology, Vol. II , pp.746-753.
30. Dilek Canakcl 2020, "Synthesis, spectroscopic, thermodynamics and kinetics analysis study of novel polymers containing various Azo chromophore", Scientific Repots nature research, https://doi.org/10.1038/s41598-019-57264-3.