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# STUDIES OF THERMAL DECOMPOSITION IN SnSe AND $SnSeCu_{0.02}$ SINGLE CRYSTALS

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**Abstract**: SnSe and $SnSeCu_{0.02}$ single crystals have been grown by a Direct Vapour Transport technique to save the grown material from the contamination of the transporting agent. The Energy Dispersion Analysis of X-rays of the as grown crystals have shown them to be in perfect stoichiometry. The powder X-ray diffraction pattern of grown crystals confirmed orthorhombic structure with lattice parameters which nearly match with the reported values. In order to make the grown material suitable for device applications, it is necessary to test them for their thermal stability. Therefore, thermogravimetric (TG), differential thermal (DTA) and differential thermogravimetric (DTG) analyses of the as grown crystals of SnSe and SnSeCu0.02 in air showed them to be stable in the temperature range of ambient to 1001 K for SnSe and from ambient to 1064 K for SnSeCu0.02. The activation energy (Ea), activation enthalpy ($\Delta H^*$), activation entropy ($\Delta S^*$) & Gibbs free energy change ($\Delta G^*$) of SnSe & SnSeCu0.02 single crystals were determined from the thermal curves using the four standard relations. The implications of our findings have been discussed here.

**Keywords:** Thermogravimetric (TG) analyses, differential thermal (DTA) analyses, Differential thermogravimetric (DTG) analyses, activation energy, BR relation, HM relation, PN relation, CR relation, activation enthalpy ($\Delta H^*$), activation entropy ($\Delta S^*$), Gibb's free energy change ($\Delta G^*$).

**Mathematics Subject Classification: 74A15, 80A20, 80A30, 74E15, 74F05**

## 1. Introduction

Tin based Sn-X (X = S, Se, Te) chalogenide compounds have been studied because of their potential applications in electronic, optical, opto-electronic and flexible systems. Among the family of Sn – X materials, tin selenide (SnSe) is a material which consists of non-toxic and economical earth abundant elements. SnSe possesses a layered

orthorhombic structure having a space group Pnma. The structure consists of strongly bound double layers and can be considered as a distorted rock salt phase. SnSe is a material which can work excellently for photovoltaic and optoelectronic applications because of proper energy band structure and electronic properties [7, 6]. Recently Zhao et al [9] showed that SnSe can act as a superior thermoelectric material due to dimensionless figure of merit ZT~2.6. It becomes therefore essential to study the thermal stability of this material before making its use in any device. Author has therefore carried out a systematic study of the thermal properties of SnSe and $SnSeCu_{0.02}$ single crystals. Both these crystals have been grown by a direct vapour transport technique to avoid their contamination from the transporting agent. The thermal properties have been studied by recording curves for thermo gravimetric (TG), differential thermo gravimetric (DTG) and differential thermal analysis (DTA). The kinetic and thermo gravimetric parameters such as activation energy, entropy, enthalpy and Gibb's free energy have been calculated from the TGA, DTA and DTG curves employing four standard relations for SnSe and $SnSeCu_{0.02}$ single crystals.

## 2. Experimental

SnSe and $SnSeCu_{0.02}$ single crystals were grown by the direct vapour transport (DVT) technique. The compositional characterization of the grown crystals was done by EDAX employing NOVA NANOSEM 450 scanning electron microscope and structural characterization was carried out by X ray diffraction (XRD) using Philips Xpert MPD X ray diffractometer. The TGA, DTG and DTA curves were simultaneously recorded for the grown crystals of SnSe and $SnSeCu_{0.02}$ using SEIKO EX STAR 511 TG/DTA 7200 thermal analyzer. All the thermo curves were recorded in the temperature range from ambient to 1233 K in the open air. The thermo curves for SnSe was recorded for a heating rate of 288 K per minute and for $SnSeCu_{0.02}$ the heating rate was 283 K per minute. The sample mass for SnSe was 4.642 mg and for $SnSeCu_{0.02}$ it was 12.646 mg. The kinetic parameters were calculated using the data obtained from the thermo curves using the four standard relations described below.

### 2.1 Broido relation [1]

The TG curve for a decomposition reaction can be given as

$$\ln \frac{1}{y} = \frac{K_0}{\alpha} \int_{T_0}^{T} e^{\frac{-E}{RT}} dt \tag{1}$$

Where $\alpha$ is the heating rate, y is the fraction of the initial material not yet decomposed, $K_0$ is pre exponential factor (also called as Arrhenius constant-A) is assumed to be independent of temperature, E is activation energy, T is absolute temperature and R is universal gas constant (8.314 J/mol.K).

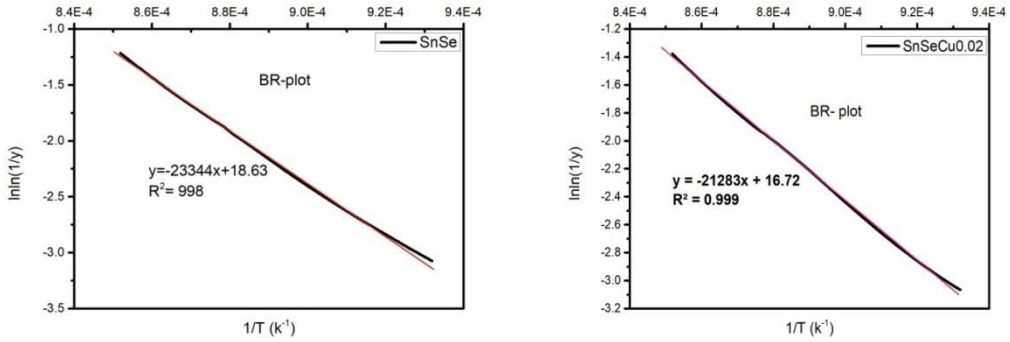


**Fig. 1. Broido(BR) plot for (a) SnSe and (b) $SnSeCu_{0.02}$ (1073 – 1173 K)**

It is seen that almost the entire measurable reaction occurs within the temperature range 800 - 900 $^{o}$C (1073 K – 1173 K).

Thus we get

$$\ln(\ln\frac{1}{y}) = \left(\frac{E}{RT_m^2}\right)T + CONSTANT \tag{2}$$

Here $T_m$ is the temperature of the maximum decomposition rate. Its value can be obtained from the DTA peak position. From the slope of the straight line plot of the $\ln(\ln\frac{1}{y})$ vs $\frac{1}{T}$ (**Fig.1.**), the value of activation energy can be calculated for SnSe and $SnSeCu_{0.02.}$ as shown in Table 3.

**2.2 Horowitz - Metzger (H-M) relation [4]**

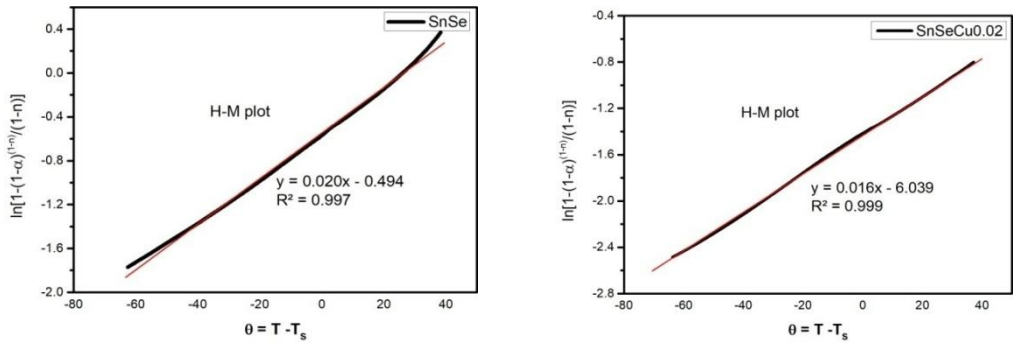


**Fig. 2. H-M plot for (a) SnSe and (b) $SnSeCu_{0.02}$ (1073 – 1173 K)**

At the temperature $T_m$ at which the maximum decomposition take place, the equation for the thermo gravimetric trace can be written as

$$\ln\left[\frac{1-\left(1-\alpha^{(1-n)}\right)}{1-n}\right] = \frac{E\theta}{RT_m^2} \tag{3}$$

Where n≠1 i.e n = 1/2, 1/4, 2/3 etc.

From the plot of $\ln\left[\frac{1-(1-\alpha)^{(1-n)}}{1-n}\right]$ vs θ for SnSe and $SnSeCu_{0.02}$ (**Fig.2.**), the activation energy can be obtained and the results are shown in the Table 3.

### 2.3 Piloyan-Novikova (PN) relation [5]

According to PN relation, the dissociation rate can be obtain from the equation

$$\ln\left(\frac{\alpha}{T^2}\right) = \ln\left(\frac{ZR}{E\beta}\right) - \frac{E}{RT} \tag{4}$$

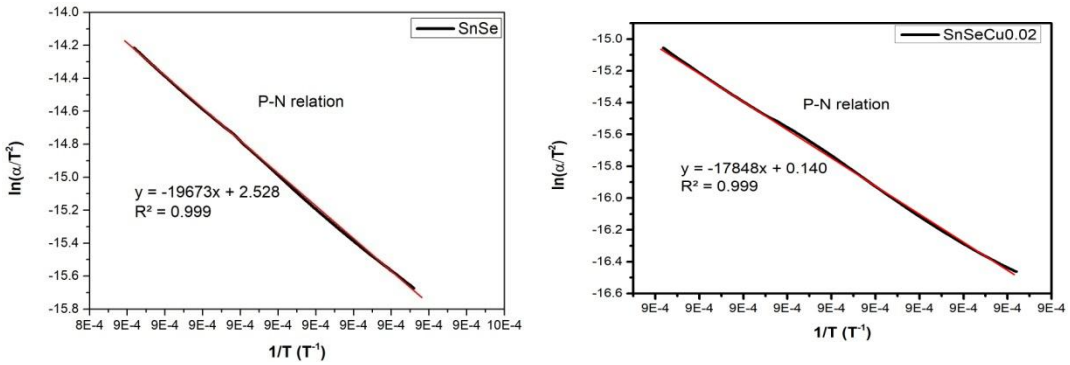


**Fig. 3. P-N plot for SnSe and $SnSeCu_{0.02}$ (1073 – 1173 K)**

The activation energy for SnSe and $SnSeCu_{0.02}$ has been calculated from the straight line plot of $\ln\left(\frac{\alpha}{T^2}\right)$ vs $\frac{1}{T}$ (**Fig.3.**). The results thus obtained are given in table 3.

### 2.4 Coats-Redfern (C-R) relation [3]

We have also used C-R relation for evaluation of activation energy.

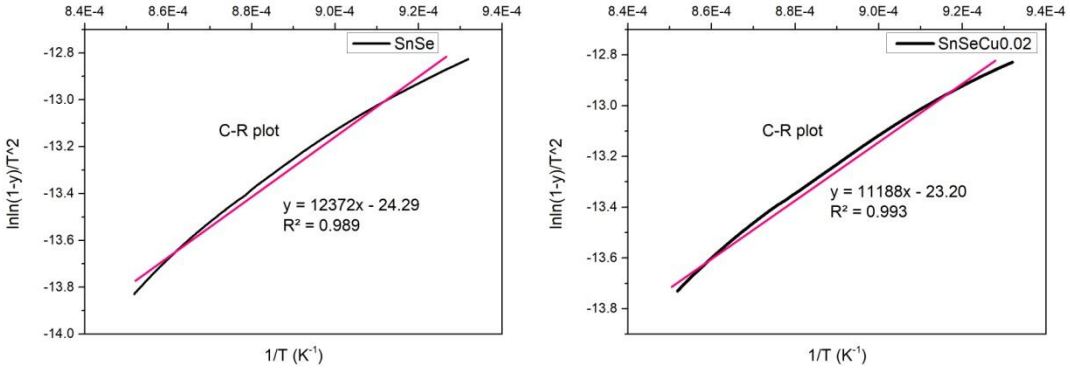


**Fig. 4. C-R plot for SnSe and $SnSeCu_{0.02}$ (1073 – 1173 K)**

The Thermo gravimetric data can be used to evaluate kinetic parameters of reactions involving weight loss (or gain) from the relation

$$a\ A_{(s)} \rightarrow bB_{(s)} + cC_{(g)} \quad (5)$$

The disappearance rate of A can be expressed as

$$\ln\left[\frac{-\ln(1-y)}{T^2}\right] = \ln\frac{ZR}{E\beta} - \frac{E}{RT} \quad (6)$$

The activation energy for SnSe and $SnSeCu_{0.02}$ can be obtained from the straight line plot of $\ln\left[\frac{-\ln(1-y)}{T^2}\right]$ vs $\frac{1}{T}$ (**Fig.4.**) as shown in table 3.

The other thermal parameters such as activation enthalpy ($\Delta H^*$), activation entropy ($\Delta S^*$), and Gibb's free energy change ($\Delta G^*$) for decomposition of SnSe and $SnSeCu_{0.02}$ single crystal can be calculated from the standard relations [2] given below.

$$\left(\Delta H^*\right) = E_a - RT$$

$$\left(\Delta S^*\right) = 2.303R\log\left(\frac{Ah}{K_B T}\right)$$

$$\left(\Delta G^*\right) = \Delta H^* - T\Delta S$$

Here $E_a$ is the activation energy, R is the gas constant, A is the Arrhenius constant, $K_B$ is the Boltzmann constant, h is the plank constant, T is the temperature of DTG peak.

The Thermal and kinetic parameters for SnSe and $SnSeCu_{0.02}$ are given in Table 4.

## 3. Results and Discussion

The compositional analysis of the grown crystals was made by EDAX technique. The results presented in Table 1 show that grown crystals are nearly stoichiometric.

**TABLE 1: EDAX data of grown crystals**

| SnSe | | | SnSeCu0.02 | | |
|---|---|---|---|---|---|
| Elements | wt% | standard wt% | Elements | wt% | standard wt% |
| Sn | 58.26 | 60.05 | Sn | 57.89 | 59.67 |
| Se | 41.74 | 39.95 | Se | 41.82 | 39.69 |
| | | | Cu | 0.59 | 0.64 |

The lattice parameters shown in Table 2 were determined from the X-ray diffraction. The observed values match with those reported in literature [8].

**TABLE 2. Lattice parameters of grown crystals**

| Lattice parameter | SnSe | SnSeCu0.02 |
|---|---|---|
| a (A°) | 11.515 | 11.4855 |
| b (A°) | 4.44 | 4.44 |
| c (A°) | 4.15 | 4.145 |

### 3.1 Evaluation of kinetic parameters using TG curve

The TG and DTA curves obtained for SnSe and $SnSeCu_{0.02}$ are shown in **Fig. 5.**

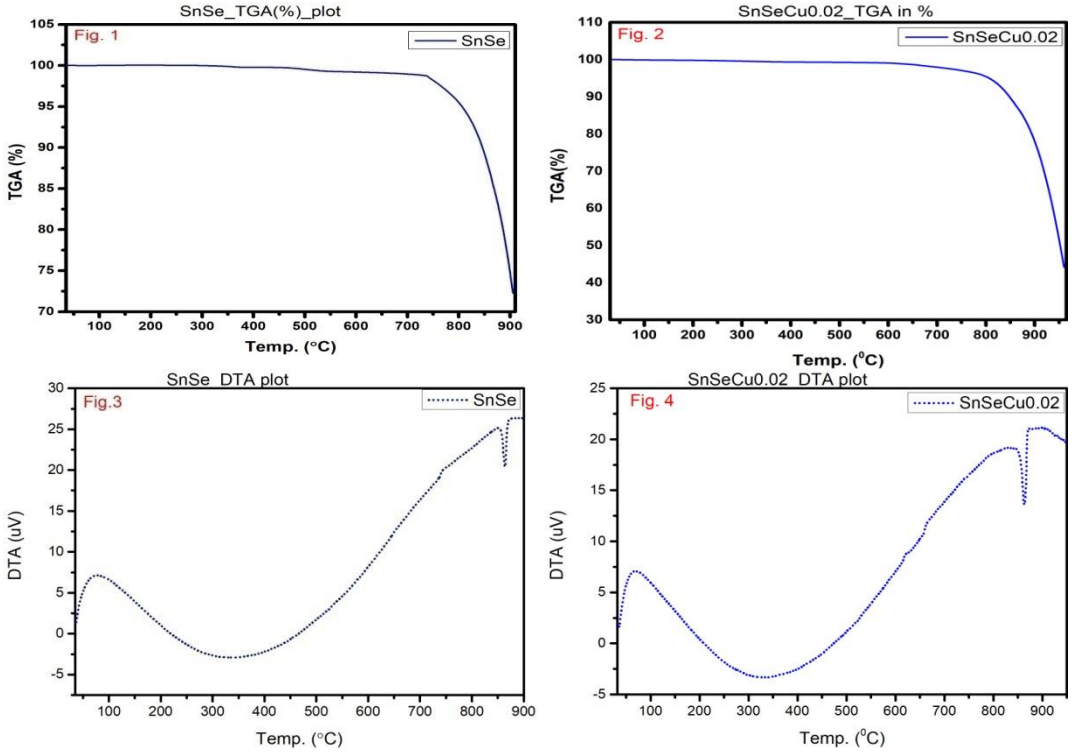


**Fig.5: (1) TGA curve for SnSe and (2) $SnSeCu_{0.02}$ single crystal (3) DTA curve for SnSe and (4) $SnSeCu_{0.02}$ single crystal**

A careful study of TG curve for SnSe (Fig.5.1) reveals that the major decomposition of the material begins at around 1001 K (728 °C) and continues upto 1173 K (900 °C). Between ambient temperature to 1001 K, the decomposition is very slow and the weight loss is too small for kinetic parameters evaluation. In the similar way the TG curve for $SnSeCu_{0.02}$(Fig.5.2) reveals that the major decomposition starts at 1161 K (888 °C) and continues upto around 1232 K (959 °C). Between ambient to 1161 K the decomposition is slow and the weight loss is too small for kinetic parameters to be evaluated. The kinetic parameters for the major decomposition from 1001 K to 1173 K for SnSe and from 1161

K to 1232 K for $SnSeCu_{0.02}$ have been calculated by four standard relations discussed earlier. The evaluated parameters are given in Tables 3 and 4.

**TABLE 3. Kinetic parameters for SnSe and SnSeCu0.02 crystals**

| TGA Temperature range (K) | DTA peak temperature (K) | Mass loss (%) | Relation used | Activation Energy ($E_a$) (joule/mole) |
|---|---|---|---|---|
| **SnSe** | | | | |
| 1073-1173 | 1135.67 | 27.77 | BR | 1.94E+05 |
| | | | HM | 2.14E+05 |
| | | | PN | 1.63E+05 |
| | | | CR | 1.03E+05 |
| **$SnSeCu_{0.02}$** | | | | |
| 1073-1173 | 1136.78 | 55.87 | BR | 1.77E+05 |
| | | | HM | 1.72E+05 |
| | | | PN | 1.48E+05 |
| | | | CR | 1.00E+05 |

The positive values of ΔH in Table 4 clearly shows that heat is absorbed by SnSe and $SnSeCu_{0.02}$ samples. This heat absorption causes decomposition of these crystal samples. This decomposition is supported by the weight loss in their TG curves. This heat absorption is also reflected in the DTA curves of these samples. The negative values of ΔS in these samples indicate that entropy is decreasing in the temperature ranges mentioned in the table. The positive values of ΔG in Table 4 clearly shows that decomposition process in these samples are non-spontaneous.

**TABLE 4 Thermogravimetric parameters for SnSe and SnSeCu0.02 crystals**

| Sample | Relation used | DTG peak temperature (K) | Pre exponential factor A ($min^{-1}$) | ΔH ($KJ.mole^{-1}$) | ΔS ($KJ.mole^{-1}$) | ΔG ($KJ.mole^{-1}$) |
|---|---|---|---|---|---|---|
| SnSe | BR | 1138.15 | 8.41E+12 | 184.64 | -8.59 | 194.40 |
| | HM | 1138.15 | 1.21E+06 | 205.01 | -499.41 | 772.18 |
| | PN | 1138.15 | 3.70E+06 | 154.04 | -129.30 | 302.01 |
| | CR | 1138.15 | 1.52E+13 | 93.37 | -3.69 | 97.56 |
| $SnSeCu_{0.02}$ | BR | 1186.94 | 4.60E+12 | 167.50 | -13.63 | 182.98 |
| | HM | 1186.94 | 2.26E+11 | 162.45 | -398.48 | 615.44 |
| | PN | 1186.94 | 2.05E+05 | 138.87 | -154.34 | 314.32 |
| | CR | 1186.94 | 9.40E-06 | 83.52 | -352.27 | 483.98 |

The TG curve of SnSe in air shows 0.3% loss from ambient to 612 K and 1.78% loss from ambient to 1001 K. In these temperature ranges, oxidation of excess selenium in the sample is taking place in air. The maximum weight loss of 27.33 % is observed in the

temperature range 1073 K- 1173 K. This weight loss can be attributed to the decomposition of SnSe crystal samples. Similar to this behavior TG curve of $SnSeCu_{0.02}$ in air shows 0.49 % weight loss from ambient to 606 K and 3.95 % loss from ambient to 1097 K. The maximum weight loss of 55.87 % is taking place in the temperature range 1073 K - 1173 K. The DTG curve in this temperature range shows two peaks which can be due to difference in decomposition of SnSe and $SnSeCu_{0.02}$ samples.

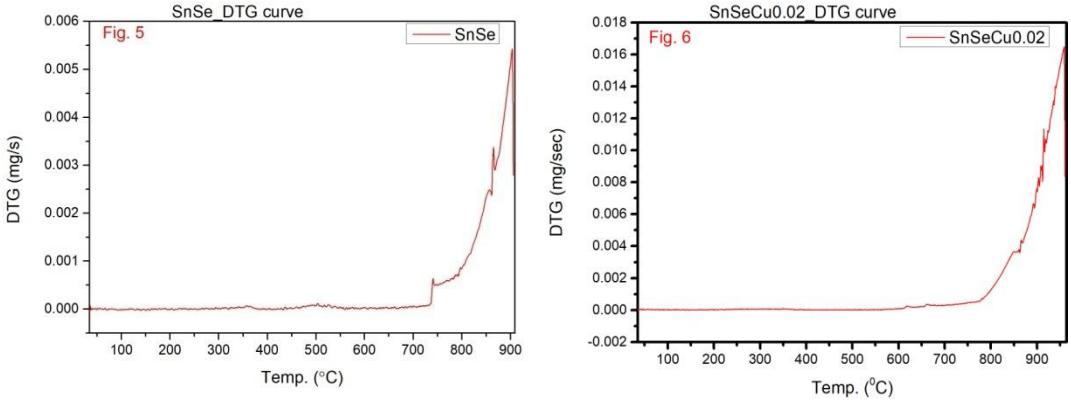


**Fig. 6:(1) DTG curve for SnSe and (2) $SnSeCu_{0.02}$ single crystal**

The simultaneously recorded DTG curve for SnSe and $SnSeCu_{0.02}$ are shown in Fig 6.1 and Fig 6.2. The DTG curve shows two peaks in the temperature range 1001-1173 K. These two peaks are not visible in the TG curve; instead we see a continuous linear weight loss behavior. It is possible that minor slope changes in TG curve give rise to these peaks in DTG. A similar story is repeated in the DTG curve for $SnSeCu_{0.02}$, but here the two peaks are observed at 1173.54 K and 1186.94 K. Similar to SnSe here also these two peaks are missing in the TG curve.

The DTA curve shown in Fig. 5.3 for SnSe shows exothermic behavior between ambient to 351 K followed by an endothermic reaction between 351 K - 613 K and thereafter by an exothermic reaction reaction between 613 K – 1123 K. After that again from 1123 K - 1134.5 K and above the behavior is first exothermic and then endothermic. The initial exothermic reaction is due to formation of water vapour by trapped water. The endothermic reaction between 351 – 613 K indicates absorption of heat which is used for oxidation of excess selenium in air. This oxidation leads to a negligible weight loss in the sample. The presence of excess amount of Se in the sample can be checked from its EDAX analysis. This fact can be confirmed from the TGA curve in this region. The release of heat shown by exothermic nature of the DTA curve in the range 613 K – 1123 K is due to the loss of heat caused by the decomposition of the sample. This fact is supported by the loss of weight of 10.17 % seen in the TGA curve. in this temperature range.

The DTA curve in Fig.5.4 for $SnSeCu_{0.02}$ can be divided into five temperature ranges as shown in Table 5 below. The nature of reaction exhibited by the curves in these regions is also reported in this table.

**TABLE 5 Temperature ranges for SnSeCu0.02 crystals in DTA curve**

| Temperature range (K) | Nature of reaction |
|---|---|
| Ambient to 343 K | exothermic |
| 343 – 606 K | endothermic |
| 606 – 1097 K | exothermic |
| 1097- 1143 K | endothermic |
| Above 1143 K | exothermic |

This explanation for exothermic and endothermic reactions in $SnSeCu_{0.02}$ is similar to SnSe except one difference that reaction shown by the curve above 1097 K is due to decomposition of $SnSeCu_{0.02}$ which can be attributed to formation of SnSe and $Cu_2Se$ separately.

## 4 Conclusions

A study of thermal analysis has been made on single crystals of SnSe and $SnSeCu_{0.02}$ grown by a direct vapour transport technique. EDAX analysis of these crystals has shown them to be nearly stoichiometric without any impurity. Lattice parameters obtained from the XRD pattern of these crystals match with the values reported in the literature. The TG analysis showed that from ambient to 1001 K in SnSe and from ambient to 1064 K in $SnSeCu_{0.02}$, the single crystals of these materials suffer minor loss in weight and are therefore thermally stable in these ranges. In the DTG curves, above 1001 K in SnSe and above 1064 K in $SnSeCu_{0.02}$ the magnitude of mass loss increases which suggest decomposition of these crystals. The DTA curves of these materials showed initial minor exothermic nature followed by and an endothermic curve and finally above 606 K an exothermic nature. The initial small exothermic nature is due to conversion of entrapped water into vapour. The subsequent weight loss observed in TG curves is due to decomposition of the materials due to heating. The kinetic and thermodynamic parameters for SnSe and $SnSeCu_{0.02}$ have been determined using four standard relations. The data obtained by this analysis supports the observations reported by the thermo-curves.

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## References

[1] Broido, A.(1969). A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data, *J. Polym. Sci. B Polym. Phys.*, **7**, 1761-1773.

[2] Chaki, S.H., Deshpande, M.P. and Tailor, J.P. (2013). *AIP Conf. Proc*., **1536**, 831-832.

[3] Coats, A.W. and Redfern, J.P. (1964). Kinetic Parameters from Thermogravimetric Data, *Nature*, **201**, 68-69.

[4] Horowitz, H.H. and Metzger, G.A. (1963). A New Analysis of Thermogravimetric Traces, *Anal. Chem.*, **35(10)**, 1464-1468.

[5] Piloyan, G. O. & Novikova, O. S. (1967). DTA and TG determination of the activation energy for dissociation processes, *Russian J. Inorg. Chem*, **12**, 313-319.

[6] Reddy, N. K., Devika, M. and Gopal, E.S.R. (2015). Review on Tin (II) Sulfide (SnS) Material: Synthesis, Properties, and Applications, *Crit. Rev. Solid State Mater Sci.*, **40:6**, 359-398.

[7] Reddy, V.R.M., Gedi, S., Pejjai, B. and Park, C. (2016). Perspectives on SnSe-based thin film solar cells: a comprehensive review, *J. Mater Sci., Mater Electron*, **27**, 5491-5508.

[8] Singh, N.K., Bhatula, S., Gahtori, B., Tyagi, K., Haranath, D. and Dhar, A. (2016). The effect of doping on thermoelectric performance of p-type SnSe: Promising thermoelectric material, *J. Alloys Compd.*, **668**, 152-158.

[9] Zhao, L.D., Lo, S.H., Zhang, Y., Sun, H., Tan, G., Uher, C., Wolverto, C., Dravid, V.P. and Kanatzidis, M.G. (2014). Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals, *Nature*, **508**, 373-377.