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THERMAL DECOMPOSITION OF Pb DOPED GERMANIUM MONOSELENIDE CRYSTALS

Pratik Pataniya, G. K. Solanki*, K. D. Patel, Mohit Tannarana and C. K. Zankat
Department of Physics, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India

ABSTRACT

A systematic study on thermal properties of Pb doped germanium monoselenide crystals grown by the direct vapour transport technique is reported. The GeSePbx (x=0.02, 0.04, 0.06) crystals belong to orthorhombic structure. These compounds in the crystalline form have been subjected to the thermal decomposition at the temperature from room temperature to 890 K. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for $GeSePb_x$(x= 0.02, 0.04, 0.06)crystals in inert nitrogen atmosphere. The thermal kinetic parameters of these compounds were determined from the thermal curves using Broido and Coats - Redfern relations.

Keywords:Crystal growth,activation energy, activation entropy, activation enthalpy.

INTRODUCTION

Transition metal chalcogenideshave played vital role because of their wide applications as catalysts in various chemical processes. Germanium monoselenide belong to the family of IV-VI chalcogenide semiconductors with orthorhombic structure (Pnmc) [1].Their structure may also be considered as distorted NaCl structure. This type of structure is of particular interest due to the arrangement of the cations and anions within the structure lattice. The layers of cations are separated by Van der Wall'sforces, which provide a chemically inert surface free from dangling bonds and surface density of state. Consequently, there is no Fermi level pinning at the semiconductor surface. This fact leads to a considerably high chemical and environmental stability [2,3]. These layered materials also play a key role in high pressure solid state lubrication [4, 5], electrode material in solar energy conversion devices [2] and primary and secondary batteries [6-8]. Discovery of mechanical exfoliation technique for the graphene opens up tremendous opportunities for re-engineering the various properties of the layered TMCs [9-11]. The lattice parameters of crystalline GeSe are a=3.82Å, b=4.14Åand c=10.862Å. Its unit cell contains eight atoms organized into two adjacent double layers that are perpendicular to c-axis. In each double layer, a single Ge atom attached with its three nearest Se atoms by covalent bonds and form zigzag chain along a or b- axis of crystal[12]. The presence of van der Waals gaps between these double layersallows one to exfoliate crystals into its building blocks.

Thermal analysis is a process in which a physical property of the sample is measured as a function of temperature.These techniques include Thermal Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Differential Thermal Gravimetry(DTG) [13]. In TGA, mass of the sample in an inert atmosphere is recorded as a function of temperature or time whilst the substance is subjected to a controlled temperature program and it is commonly employed in research to determine the degradation temperature and kinetic parameters [14, 15]. DTA is a technique in which the potential difference (ΔT) between the sample under study and reference is measured as a function of temperature [16]. In addition, DTA and various thermo-analytical methods can be used to study structure and behavior of samples. Further, thermo dynamical parameters such as energy of activation, enthalpy of activation, entropy of activation and free energy can also be determined by different analytical methods. Hence, kinetics of chemical reaction can be studied[17, 18] by this analyses. It is most versatile process to determine Arrhenius constant, which is also known as pre-exponential or frequency factor. Keeping all these aspects in mind, thermal decomposition of $GeSePb_x$ (x=0.02, 0.04, 0.06) compounds have been examined.

EXPERIMENTAL

The crystals of $GeSePb_x$ (x= 0.02, 0.04, 0.06) shown in Fig. 1 were grown by the direct vapour transport technique using constituent elements of 99.99% purity. The complete details of growth parameters are summarized in Table: 1. Thermal analysis was performed by recording TGA/DTG and DTA curves of these crystals by SII-EXSTAR TG/DTA-7200 in N_2 atmosphere. The experiments were performed from ambient temperature to 890 K for all the crystals at heating rate of 10ºC/min.The above mentioned kinetic parameters were calculated from the maximum weight loss using Broido (B-R) [19] and Coats – Redfern (C-R) relation [20]. The presently calculated values of the kinetic parameters are tabulated in Table 2 for all compounds.

Table 1: Growth parameters for $GeSePb_x$ (x= 0.02, 0.04, 0.06) crystals.

Growth Parameters		$GeSePb_x$ (x= 0.02, 0.04, 0.06)		
		x = 0.02	x = 0.04	x = 0.06
Temperature (K)	Source Zone	873	873	873
	Growth Zone	823	823	823
Growth Periods (hour)		80	80	80
Crystal Dimensions (mm × mm)		15 × 8	12 × 8	16 × 8
Physical Appearance		Shiny Gray	Shiny Gray	Shiny Gray

*Corresponding author: *solankigunvant@yahoo.co.in*

Fig:1.Photographs of grownGeSePb$_x$ (x=0.02, 0.04, 0.06) crystals

RESULTS AND DISCUSSION

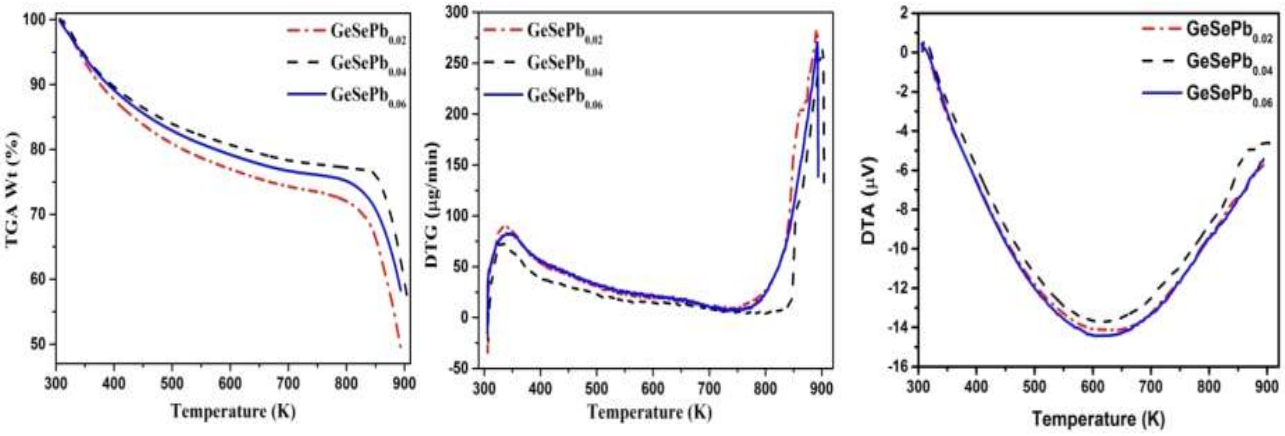

Fig:2.Various thermal curves of GeSePbx (x= 0.02, 0.04, 0.06) crystals.

As shown in Fig. 2, TGA, DTG and DTA curvesrecorded for GeSePb$_x$ (x=0.02, 0.04, 0.06) illustrate thermal decomposition in N2 atmosphere. TGA curve shows a single step of dissociation from 845-893 K. The first zone of DTG curve from 308-473K correspond to the removal of some volatiles (i.e. oxygen, etc.) present on surface of crystals. The presence of similar region between 473K and 773K in TGA shows no significant weight loss, thus supporting the conjecture that all samples have thermally stable composition. However, presence of unreacted selenium causes trivial weight loss in all compounds between 473K and 573K.The grown GeSePb$_x$ (x=0.02, 0.04, 0.06) compounds decomposes in single step and maximum weight loss occur at 858K, 863K and 883K, respectively. The total weight loss for grown samples is also summarized in Table 2.As shown in Fig. 2, DTA curves for grown samples confirm that the decomposition is endothermic and non-spontaneous.

EVALUATION OF KINETIC PARAMETERS

The TGA is expedient technique for evaluation of kinetic parameters of various materials that in turn provides valuable quantitative information regarding the stability of the materials. Various methods have been proposed to estimate the kinetic parameters for thermal decomposition. In the preset work, Broido and Coats-Redfern methods have been employed for estimation.

BROIDO METHOD

The rate of dissociation is given by the kinetic relation,

$$\ln\left(\ln\frac{1}{Y}\right) = \ln\frac{AR}{Eb} - \frac{E}{RT} \qquad (1)$$

where, 'Y' is dissociation rate, 'E' is the activation energy (kJ/mol), 'β' is heating rate (°C/min), R is universal gas constant (8.314 J/K mol) and 'A' is the frequency factor or pre-exponential factor (s-1).

The activation energy and pre-exponential factor have been calculated from slope and intercept of the best fit curve of ln(ln(1/Y)) vs 1/T(Fig. 3), respectively. The calculated values of activation energies and pre-exponential factors for all compounds are summarized in Table 2.

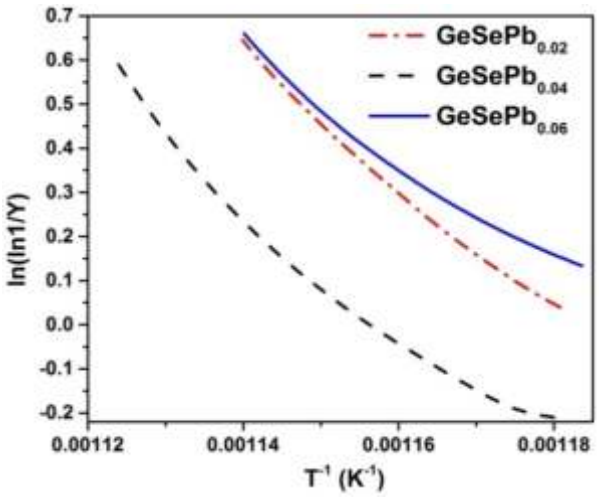

Fig:3. BR plots for $GeSePb_x$ (x = 0.02, 0.04, 0.06) crystals.

COATS-REDFERN METHOD

Similarly, kinetic parameters have also been determined by employing C-R relation. From the following relation:

$$aA_{(s)} \rightleftharpoons bB_{(s)} + cC_{(g)}$$

The rate of disappearance of A may be written as

$$\log \frac{-\log g(\alpha)}{T^2} = \log \frac{ZR}{Eb} - \frac{E}{2.303RT} \qquad (2)$$

With,

$$g(\alpha) = \frac{(W_\alpha - W)}{W}$$

where, W_α is the mass lose in reaction and W is the mass lose at absolute temperature T. The straight line plot of $\log(-\log g(\alpha)/T^2)$ vs 1/T(Fig.4) gives the values of the activation energy (E) and pre-exponential factor (A).

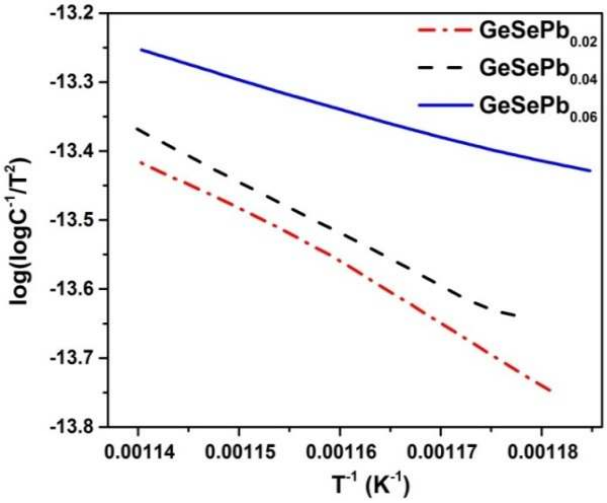

Fig:4. CR plots for $GeSePb_x$ (x= 0.02, 0.04, 0.06) crystals.

The activation enthalpy (ΔH), activation entropy (ΔS) and activation Gibbs free energy change (ΔG) of $GeSePb_x$ (x=0.02, 0.04, 0.06) crystals were calculated using the following relations [21]:

$$\Delta H = E - RT \qquad (3)$$

$$\Delta S = 2.303R \log\left(\frac{Ah}{kT}\right) \qquad (4)$$

$$\Delta G = \Delta H - T\Delta S \qquad (5)$$

where, 'E' is activation energy, 'A' is Arrhenius constant, 'k' is Boltzmann constant and 'h' is Planck'sconstant.

The data obtained from above analysis are given in Table 2 for decomposition of $GeSePb_x$ (x=0.02, 0.04, 0.06) samples. It can be concluded that the higher values of activation energies confirm the crystalline nature of grown samples. It was observed that activation energy decreases as lead content increases in grown compounds that in turn predict the decrease in crystalline nature. The entropy of activation shows negative values which indicate more randomness within the system and it also suggest that thermal decomposition is slow. The entropy of activation become more negative as lead content increases in grown samples i.e. randomness increases. Hence composition with highest concentration of lead ($GeSePb_{0.06}$) is least crystalline. Further, the positive values of activation enthalpy indicate that the heat is being absorbed in the dissociation and the reaction is endothermic in nature. The positive values of activation free energy state that the dissociation process is non-spontaneous. Further, the higher values of ΔG explain more endothermic and slower dissociation of $GeSePb_x$ (x=0.02, 0.04, 0.06) compound.

CONCLUSIONS

The crystals of $GeSePb_x$ (x=0.02, 0.04, 0.06) have been grown by the direct vapour transport technique in the platelets form having thickness of few microns. The thermal stability of $GeSePb_x$ (x=0.02, 0.04, 0.06) crystals were studied using different thermal techniques. The thermal stability of samples seems to be decrease with increase in lead contentin grown crystals. Various kinetic parameters like activation energy, enthalpy, entropy and Gibbs free energy have been determined from TGA curve using B-R and C-R-relation.

Table: 2. Kinetic parameters for GeSePbx(x= 0.02, 0.04, 0.06) crystals.

Crystals	T (K)	T_P (K)	Wt% Loss	Relation used	E (kJ/mol)	ln A	ΔH (kJ/mol)	ΔS (J/K mol)	ΔG (kJ/mol)
$GeSePb_{0.02}$	847-873	858	50.7	CR	158.04	20.31	150.52	-84.89	223.36
				BR	122.68	15.45	115.57	-125.31	222.83
$GeSePb_{0.04}$	846-878	863	42.5	CR	142.62	18.23	135.23	-102.16	223.39
				BR	117.14	14.54	109.97	-132.95	224.71
$GeSePb_{0.06}$	845-877	883	41.8	CR	77.09	10.03	81.67	-170.65	232.36
				BR	98.60	11.95	91.43	-154.24	224.54

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