On the crystallization kinetics of multicomponent nano-chalcogenide \( \text{Se}_{79-x}\text{Te}_{15}\text{In}_6\text{Pb}_x \) (\( x = 0, 1, 2, 4, 6, 8 \) and 10) alloys

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Abstract

Nanotechnology continuously rises due to its potential applications. To control nano-materials design and microstructure, it is very essential to understand nucleation and crystalline growth in these materials. In this research contribution, crystallization kinetics and thermal behaviour of nano-crystalline \( \text{Se}_{79-x}\text{Te}_{15}\text{In}_6\text{Pb}_x \) (\( x = 0, 1, 2, 4, 6, 8 \) and 10 at. wt\%) chalcogenide alloys is analyzed through differential scanning calorimetry (DSC) process under non-isothermal conditions at four different heating rates; 5, 10, 15 and 20 °C min\(^{-1}\). The examined Se-Te-In-Pb nano-chalcogenide system is prepared through melt-quenching process. Characteristic temperatures namely glass transition temperature (\( T_g \)), onset crystallization temperature (\( T_o \)), peak temperature of crystallization (\( T_p \)) and melting temperature (\( T_m \)) show dependence on heating rate and composition. The various kinetic parameters such as activation energy of glass transition (\( E_g \)), activation energy of crystallization (\( E_c \)), reduced glass transition temperature (\( T_{rg} \)), Hruby number (\( K_{p0} \)), thermal stability parameters (\( S \) and \( H \)) and fragility index (\( F_i \)) are analyzed for investigated Se-Te-In-Pb nano-crystalline system. Different empirical approaches are applied to determine the apparent glass transition activation energy (\( E_g \)) and crystallization activation energy (\( E_c \)).

1. Introduction

The advancement in characterization and visualization techniques opens up a new window in materials science for control synthesis of materials at nano-level. The nanostructure configurations are progressively attracting huge attention not only for basic research point of view but for their unique properties; electronic, optical, large surface-to-volume ratio etc as compared to bulk systems [1, 2]. Nanostructure synthesis has been analyzed for several materials and interest has been developed in nano-crystalline Pb-chalcogenide semiconductors because of size tuneable properties occurring due to quantum confinement [3, 4]. They have potential applications as solar conversion devices, photo-sensors, and detectors of infrared radiation, photo resistors, photo detectors, nonlinear optical devices, thermo-electric devices, lasers, infrared emitters and solar control coatings [5–7].

A lot of research is focused on fundamental issues of these metal-containing nano-crystalline materials due to their unusual properties, including chemical durability, anomalous order of band-gaps, large dielectric constant, high carrier mobility, low phonon energy, extended IR transparency, large photo sensitivity, special nonlinear optical properties and high thermal stability [2, 8–14]. The multi-component chalcogenide nano-crystals proposed excessive assistance of having tuneable electronic, optical, defect and structural properties which facilitate photovoltaic characteristics [12]. All these fascinating, attractive and unique properties of Pb additive nano-structured semiconductors have prompted scientists to explore fundamental properties of these systems and there is a lot of scope for studying these materials in nano-range.

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Chalcogenide, mostly Se-based alloys have been tremendously used in synthesis of various nano-tubes, nano-wire and nano-particles [15, 16]. Although, for technological appliances, these Se based system have limited reversibility and found to be thermally unstable [2]. Among these glasses, binary Se-Te system has gained superiority over pure amorphous Se due to their different parameters like higher crystallization temperature, higher conductivity, greater hardness, smaller ageing effect and higher sensitivity [17]. But, for practical applications these Se-Te alloys must be thermally stable with temperature and time during use. Thermal instability leads to crystallization is one of limitation of these chalcogenides systems [18]. However, addition of dopant is most efficient technique for fabricating new alloys having improved properties [19, 20]. The insertion of indium in Se-Te glassy system produces thermally stable system, thus, increases the crystallization temperature and glass transition temperature by getting cross linked structure and creating configurational and compositional disorder [21, 22]. Fundamental interest in multi-component quaternary chalcogenide alloys has been revived due to observation of quick reversible laser-induced amorphous to crystalline and crystalline to amorphous phase transitions [2]. In device fabrication, optical gap and lattice perfection plays an important role to enhance the proficiency; which depends on insertion of dopant like Pb. In certain chalcogenide systems, addition of element like Pb will cause \( p \) to \( n \) transition by limiting molecular mobility, connecting neighbouring chains and enhancing valance alteration pair (VAP) type defects [2, 17]. Pb addition to Se-based system; enhances glass forming ability, reduces aging effect and produces thermally stable system by affecting their bonding network. Pb doping prominently impacts its structural, physical, optical, electronic and thermal properties [23, 24]. All these eminent features of Pb make it attractive among the doping element in case of chalcogenide semiconductors. Our previous work on ternary Se-Te-In composition illustrates that \( \text{Se}_{79}\text{Te}_{15}\text{In}_{6} \) has higher thermal stability among investigated alloys [18, 21]. Furthermore, our earlier analysis on dielectric and AC conductivity measurement in Se-Te-Pb system signifies considerable influence of Pb doping on conduction mechanism [2, 17]. Recently, intermediate phases are observed in chalcogenide glasses; which correspond to a glassy composition having an ideal stress free network and whose glass-forming tendency is optimized [25, 26].

In nano-scale devices fabrication, the synthesis of nano-structured materials by economic and simple methods becomes an importance issue. To synthesize mono-disperse, high quality, tuneable size and shape nano-crystals; it is very essential to understand the nucleation and crystalline growth in these materials [13, 14]. The crystallization kinetics of nano-chalcogenide systems plays an important role in analyzing the thermal stability, transport mechanisms, glass forming ability and thus eventually to determine the suitable range of operating temperature for a specific technological application before crystallization takes place [27].

In present research paper, the effect of Pb additive has been analyzed in term of amorphous-crystallization transformation, thermal stability, glass transition, glass forming ability of nano-chalcogenide \( \text{Se}_{79-x}\text{Te}_{15}\text{In}_{x}\text{Pb}_{x} \) \( (x = 0, 1, 2, 4, 6, 8 \text{ and } 10 \text{ at. wt\%}) \) alloys using DSC technique under non-isothermal conditions at four heating rates viz 5, 10, 15 and 20 °C min\(^{-1}\). 

2. Experimental details

Nano-chalcogenide \( \text{Se}_{79-x}\text{Te}_{15}\text{In}_{x}\text{Pb}_{x} \) \( (x = 0, 1, 2, 4, 6, 8 \text{ and } 10 \text{ at. wt\%}) \) alloys were synthesized with melt quenching process. Pure (99.999%) elements as per at.
wt% are pondered with accuracy \( 10^{-4} \) g and sealed in (length \(~5\) cm, diameter \(~12\) mm) quartz ampoule under a vacuum \(~2 \times 10^{-5} \) mbar. Heating of sealed ampoules is done for 10 h at 3–4 °C min\(^{-1}\) heating rate up to 900 °C. Ampoules were frequently rocked for making melt homogenous at maximum temperature. The molten ampoule is quenched in ice cooled water. Deduced samples were grind into a fine powder.

Structural characterization is performed at room temperature by taking X-ray diffraction of investigated composition. The analysis of intense characteristics peaks in X-ray pattern illustrates nano-nature of studied composition further confirmed by field emission scanning electron microscope [2, 15].

The thermal behaviour of examined composition is analyzed through temperature modulated differential scanning calorimeter (TA instrument, DSC 2910). The precision of heat flow is ±0.01 mW and precision of temperature is ±0.1 °C as deduced by microprocessor of thermal analyzer. A standard aluminium pan has been used to encapsulate a sample of around 3–5 mg at a flow of 40 ml min\(^{-1}\) under dry nitrogen atmosphere. Samples are reheated at heating rates of 5, 10, 15 and 20 °C min\(^{-1}\). Characteristic temperatures; glass transition temperature \( (T_g) \), peak temperature of crystallization \( (T_p) \) and melting temperature \( (T_m) \) are deduced with microprocessor of thermal analyzer. In case of activation energies and other kinetic parameters, least-squares fitting technique is used to determine best fit of results.
3. Results and discussion

A typical DSC thermogram of Se$_{78}$Te$_{15}$In$_6$Pb$_1$ nano-chalcogenide alloy at four heating rates is given in figure 1. DSC thermogram of examined Se–Te–In–Pb nano-chalcogenide system at heating rate of 15 °C min$^{-1}$ is given in figure 2. DSC thermogram can be resolved into three main regions. The first region characterized by first endothermic peak is glass transition region, that’s arising due to rapid enhancement in specific heat of sample.
The peak value of first endotherm is denoted as \( T_m \). The second region corresponds to exothermic peak specified by crystallization process. The onset of crystallization is indicated by \( T_g \), i.e. the temperature where crystallization just starts and \( T_g \) represents peak temperature of crystallization. The third region is designated as melting temperature associated with second endothermic peak. Herein \( T_m \) corresponds to peak value of melting endotherm. It is observed that with enhancing heating rate, \( T_g \) and \( T_p \) of examined composition shift towards higher temperatures. The increase in \( T_g \) with heating rate may be attributed to relaxation dynamics in the glass transition period. \( T_g \) is the temperature at which relaxation time is equivalent to relaxation time of observation and \( T_p \) varies inversely with relaxation time [21]. Consequently when heating rate raises, \( T_g \) increase owing to reduction in relaxation time of observation. Samples primed by cooling from molten state (very high rate of cooling); associated with new degree of freedom or configuration energy states. In calorimetric analysis, samples are reheated with different heating rates, which is not similar to cooling rates during preparation. So larger is the difference, more is the structural dissimilarity among reheated solid and glass. The glassy material has ‘longer’ tendency to remain in glassy state if reheating rate is faster; which corresponds to a higher \( T_g \) [28]. \( T_p \) is found to shift towards higher temperature with heating rate. This can be explained as due to high heating rate system doesn’t have enough time for crystallization and nucleation; which cause shifting towards higher temperature [29]. The values of \( T_g \), \( T_m \), \( T_p \) and \( T_m \) at all heating rates are determined for each examined alloy. The outcomes show that 1 at wt\% Pb alloy has a higher \( T_p \). An alloy with higher \( T_p \) value has maximum operation temperature, consequently increases the archival life time [30]. Therefore, 1 at wt\% Pb system have higher value of crystallization temperature, which attributes to a single phase homogeneous morphology as confirm from DSC [30]. It is found that 10 at wt\% Pb alloy has a lower \( T_m \) value. As lower value of melting temperature reduces the RESET current and this material is advantageous in phase change random access memory (PCRAM) devices [30].

### 3.1. Glass transition activation energy

\( T_g \) reveals information about rigidity and strength of glassy network [31]. The glass transition region has been analyzed in terms of glass transition activation energy \( (E_g) \) and variation of \( T_g \) with heating rate. Lasocka suggested empirical relation [31] which relates \( T_g \) with heating rate as given below:

\[
T_g = A + B \ln(\alpha)
\]

where \( A \) and \( B \) are constants depending on glassy system and \( \alpha \) signifies heating rate. \( A \) denotes glass transition temperature at 1 K/min heating rate and within glass transition region, the time response of configurational changes with heating rate is determined by \( B \). \( T_g \) variation with \( \ln(\alpha) \) is shown in figure 3 for investigated \( \text{Se}_{79-x}\text{Te}_{15}\text{In}_6\text{Pb}_x \) \( (x = 0, 1, 2, 4, 6, 8 \text{ and } 10) \) nano-chalcogenide alloys. According to equation (1), plot among \( \ln(\alpha) \) versus \( T_g \) should be straight line and holds true for investigated chalcogenide system. The constant \( A \) and \( B \) are deduced from intercept and slope of \( T_g \) versus \( \ln(\alpha) \) plot respectively and tabulated in table 1. As cooling rate of melt is connected with constant \( B \); so lesser is the value of \( B \), lower is cooling rate of melt. Consequently, physical significance of \( B \) lies in configurational modification in glass transformation region [32]. As for studied nano-chalcogenide materials the values of \( B \) (given in table 1) are different; which illustrates that investigated systems undergoes different structural changes.

![Figure 3. Plots of \( T_g \) versus \( \ln(\alpha) \) for glassy \( \text{Se}_{79-x}\text{Te}_{15}\text{In}_6\text{Pb}_x \) \( (x = 0, 1, 2, 4, 6, 8 \text{ and } 10) \) nano-crystalline compositions.](image-url)
In second approach, the apparent $E_g$ for investigated composition has been determined using Kissinger’s equation $^{33, 34}$. As in crystallization process the activation energy is most offend determined by Kissinger equation. However it is indicated $^{35}$ that same equation can be utilized for evaluation of $E_g$, which is written as $^{32}$:

$$\ln\left(\frac{\alpha}{T^2_g}\right) = -\frac{E_g}{RT_g} + \text{constant} \quad (2)$$
where $R$ is universal gas constant. Apparent value of $E_g$ is calculated from slope of $\ln(\alpha/T_g)^2$ with $1/T_g$ plot (figure 4). The deduced values of $E_g$ for examined system are given in table 1. In addition, when alteration in $1/T_g^2$ versus $\ln(\alpha)$ is so slower as compare to alteration of $1/T_g$ versus $\ln(\alpha)$, $E_g$ can be more simplified and estimated by Moynihan et al.\[36\] formulation. Moynihan and co-workers\[37, 38\] use the theory of structural relaxation for evaluating $E_g$ through heating rate dependence of $T_g$, which is deduced by relation:

$$\ln(\alpha) = -E_g/RT_g + \text{constant}$$

(3)

Slope of $\ln(\alpha)$ with $1/T_g^2$ plot gives $E_g$ and the calculated values of $E_g$ are listed in table 1. For the investigated nano-systems the $\ln(\alpha)$ variation against $1000/T_g$ is shown in figure 5.

$E_g$ depends on $T_g$, $\alpha$ and rearrangement of atoms around $T_g$ along with molecular motion. In glassy region, $E_g$ signifies amount of energy that required by group of atoms to jump from one metastable state to another \[32\]. This means $E_g$ is responsible for rearrangement and molecular motion of atoms in region of $T_g$\[39\]. So, atom having minimum $E_g$ value has larger probability to occupy lower internal energy metastable state, which is a most stable state. Moreover outcome shows that Se$_{70}$Te$_{15}$In$_{15}$Pb$_{5}$ alloy have minimum value of $E_g$. Consequently this composition is the most stable among the investigated alloys. It is observed that values of $E_g$ estimated by Moynihan’s relation as well as Kissinger’s equation are in good agreement with each other. This indicates that in the glass transition region either of two relations can be used to calculate $E_g$.
Table 2. The crystallization activation energy ($E_c$) for glassy Se$_{79-x}$Te$_{15}$In$_{6}$Pb$_x$ ($x = 0, 1, 2, 4, 6, 8$ and $10$ at. wt%) nano-crystalline composition deduced using different methods.

| Composition     | Kissinger’s method ($E_c$ (kJ mol$^{-1}$)) | Mahadevan et al ($E_c$ (kJ mol$^{-1}$)) | Augis and Bennett method ($E_c$ (kJ mol$^{-1}$), $\ln(K_o)$, $K_o$ (min$^{-1}$)) | Augis and Bennett Approximation ($E_c$ (kJ mol$^{-1}$)) |
|-----------------|-------------------------------------------|--------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------|
| Se$_{79}$Te$_{15}$In$_{6}$ | 194.16 ± 8.51                            | 200.16 ± 8.51                       | 179.20 ± 8.44, 54.09 ± 25.19, 3.10 × 10$^{13}$ | 203.60 ± 9.27                                   |
| Se$_{79}$Te$_{15}$In$_{6}$Pb$_1$ | 117.27 ± 0.93                            | 123.78 ± 0.93                       | 111.13 ± 0.94, 33.37 ± 2.41, 3.10 × 10$^{14}$ | 119.84 ± 2.57                                   |
| Se$_{79}$Te$_{15}$In$_{6}$Pb$_2$ | 97.34 ± 0.21                             | 103.72 ± 0.21                       | 81.81 ± 0.95, 25.07 ± 2.47, 7.73 × 10$^{30}$ | 120.52 ± 0.92                                   |
| Se$_{79}$Te$_{15}$In$_{6}$Pb$_4$ | 110.45 ± 0.74                            | 116.88 ± 0.74                       | 96.13 ± 1.08, 28.96 ± 2.79, 7.67 × 10$^{12}$ | 113.66 ± 0.74                                   |
| Se$_{79}$Te$_{15}$In$_{6}$Pb$_6$ | 296.47 ± 7.94                            | 302.81 ± 7.94                       | 410.73 ± 11.25, 129.49 ± 29.30, 1.66 × 10$^{30}$ | 299.64 ± 7.94                                   |
| Se$_{79}$Te$_{15}$In$_{6}$Pb$_8$ | 116.93 ± 0.38                            | 123.25 ± 0.37                       | 83.90 ± 0.88, 26.01 ± 2.30, 1.98 × 10$^{11}$ | 120.09 ± 0.38                                   |
| Se$_{79}$Te$_{15}$In$_{6}$Pb$_{10}$ | 116.45 ± 2.55                           | 122.87 ± 6.52                       | 101.73 ± 2.86, 30.76 ± 7.40, 1.07 × 10$^{36}$ | 119.66 ± 2.52                                   |

Figure 8. Plots of $\ln(\alpha/(T_p-T_a))$ versus 1000/$T_p$ for Se$_{79-x}$Te$_{15}$In$_{6}$Pb$_x$ ($x = 0, 1, 2, 4, 6, 8$ and $10$) nano-crystalline multi-component glasses.

3.2. Crystallization activation energy

In amorphous materials, nucleation and growth process are responsible to control amorphous-crystallization (a-c) transformation mechanism, which are illustrated through activation energy and dimensionality of growth process. In glassy alloys, DSC is best technique for quantitative analysis of crystallization kinetics. As pointed out in literature [18], the three activation energies has been involved in crystallization process: (a) nucleation activation energy, (b) growth activation energy and (c) whole crystallization process activation energy. Additionally, when activation energy for growth is deduced through thermal analysis, then it can be taken equal to activation energy for whole crystallization as mentioned in different works [15, 33, 40, 41]. The activation energy for a-c transformation ($E_c$) is evaluated by analyzing DSC thermograms of investigated system. $E_c$ has been evaluated from Kissinger’s equation, which gives $T_p$ variation with heating rate ($\alpha$) as below [34, 36]:

$$\ln(\alpha/(T_p-T_a)) = -E_c/RT_p + \text{constant}$$

where $E_c$ signifies activation energy of crystallization. $\ln(\alpha/(T_p^2))$ plots against $1/T_p$ are shown in figure 6. Slope of the graph among $\ln(\alpha/(T_p^2))$ with $1/T_p$ gives value of apparent $E_c$ and values are listed in table 2. If $(1/T_p^2)$ variation with $\ln(\alpha)$ is very small as compared to $(1/T_p)$ variation; Mahadevan et al [40] have approximate equation (4) in the following form:

$$\ln(\alpha) = -E_c/RT_p + \text{constant}$$

The $\ln(\alpha)$ against $1/T_p$ plot should yield straight line as indicated in figure 7. $E_c$ can be computed from the slope of plot and deduced values are tabulated in table 2.

The $E_c$ and frequency factor ($K_o$) can determine through Augis and Bennett method [42]:

$$\ln(\alpha/T_p - T_a) = -E_c/R T_p + \ln(K_o)$$

where $K_o$ denotes frequency factor. Frequency factor indicates probability of molecular collision which is effective for formation of activated complex as well as description of phase transformation. Slope of this function determine through fitting of data, calculated $E_c$ given in table 2. $K_o$ is estimated from intercept of plot.
From the outcomes, it is analyzed that $K_o$ is maximum for 6 at. wt% of Pb, which implies that Se$_{73}$Te$_{15}$In$_6$Pb$_6$ glass has maximum resistance to crystallization. Additionally, if $T_p > T_o$, then above equation reduces to the following relation:

$$\ln\left(\frac{\alpha}{T_p}\right) = \frac{E_c}{RT_p} + \text{constant}$$

Plot of $\ln(\alpha/T_p)$ with $1/T_p$ should be straight line, as revealed in figure 9. Slope of these plots provides approximated value of crystallization activation energy, listed in table 2.

Thermal analysis is used to deduce $E_c$, which is assumed to be sum of crystal growth activation energy ($E_G$) and nucleation activation energy ($E_N$) [28]. In non-isothermal process, crystallization exotherm describes growth of crystalline phase from amorphous matrix owing to huge discrepancies in latent heats of nucleation and growth along with rapid increase in temperature. Also at temperature below crystallization exotherm nucleation calorimetrically is unobservable [28]. Therefore, in examined system deduced $E_c$ values can be represent by $E_G$. $E_c$ values obtained from above mentioned route are summarized in table 2 for the investigated samples. However, there is a slight variation in value of $E_c$ deduced from different routes. This variation may be arising due to various assumptions taken during their formulations. On comparing $E_c$ deduced values through different empirical routes; it is concluded that either of these formulations can be utilized to realize $E_c$ value along with distinct precisions.

### 3.3. The ease of glass formation

In nano-chalcogenide materials analysis thermal stability and glass forming ability are fundamental issues, as these informations are essential to determine utility of investigating system as recording materials. Erasing and phase change optical recording processes are basically depends on laser induced thermal amorphization as well as crystallization of chalcogenide systems [32]. However thermal stability of glass is significant from technical point of view. The ‘two-third’ rule is excellent relationship proposed by Kauzmann [44]; which use reduced glass transition temperature ($T_{rg}$) to determine glass forming ability (i.e. $T_{rg} \geq 2/3$). $T_{rg}$ provide information regarding ease of glass formation as [44]:

| Composition         | $T_{rg}$ (K) | $(T_p - T_g)$ (K) |
|---------------------|--------------|------------------|
| Se$_{79}$Te$_{15}$In$_6$ | 0.6543       | 43.7918          |
| Se$_{78}$Te$_{15}$In$_6$Pb$_1$ | 0.6468       | 46.9289          |
| Se$_{77}$Te$_{15}$In$_6$Pb$_2$ | 0.6453       | 38.1033          |
| Se$_{75}$Te$_{15}$In$_6$Pb$_4$ | 0.6465       | 41.4443          |
| Se$_{73}$Te$_{15}$In$_6$Pb$_6$ | 0.6281       | 50.7717          |
| Se$_{71}$Te$_{15}$In$_6$Pb$_8$ | 0.6488       | 34.7882          |
| Se$_{69}$Te$_{15}$In$_6$Pb$_{10}$ | 0.6430      | 36.4482          |

In figure 9, Variation of $\ln(\alpha/T_p)$ with $1000/T_p$ for Se$_{79-x}$Te$_{15}$In$_6$Pb$_x$ ($x = 0, 1, 2, 4, 6, 8$ and $10$) multi-component glassy alloys.
Table 4. Calculated values of Hurby number ($K_{gl}$), thermal stability parameters ($S$ and $H'$) for various glassy alloys at different heating rates.

| Composition      | GFA ($K_{gl}$)          |  |  |  | H'                  | Stability factor ($S$) |
|------------------|-------------------------|---|---|---|---------------------|------------------------|
|                  | 5 K min$^{-1}$ | 10 K min$^{-1}$ | 15 K min$^{-1}$ | 20 K min$^{-1}$ | 5 K min$^{-1}$ | 10 K min$^{-1}$ | 15 K min$^{-1}$ | 20 K min$^{-1}$ | 5 K min$^{-1}$ | 10 K min$^{-1}$ | 15 K min$^{-1}$ | 20 K min$^{-1}$ |
| Se$_{79}$Te$_{15}$In$_6$ | 0.3199       | 0.3200       | 0.3254       | 0.3159       | 0.0399       | 0.0263       | 0.0229       | 0.0287       | 1.2028       | 0.8980       | 0.8289       | 0.9540       |
| Se$_{78}$Te$_{15}$In$_6$Pb$_1$ | 0.3413       | 0.3724       | 0.4042       | 0.4333       | 0.0775       | 0.0800       | 0.0851       | 0.0900       | 1.6086       | 1.7600       | 1.9402       | 2.1658       |
| Se$_{77}$Te$_{15}$In$_6$Pb$_2$ | 0.2580       | 0.3175       | 0.3235       | 0.3605       | 0.0697       | 0.0748       | 0.0791       | 0.0790       | 1.0137       | 1.3850       | 1.3747       | 1.6086       |
| Se$_{76}$Te$_{15}$In$_6$Pb$_3$ | 0.2885       | 0.3315       | 0.3458       | 0.3742       | 0.0583       | 0.0571       | 0.0596       | 0.0604       | 1.2660       | 1.4873       | 1.5484       | 1.6985       |
| Se$_{75}$Te$_{15}$In$_6$Pb$_4$ | 0.3335       | 0.2680       | 0.2698       | 0.2724       | 0.0784       | 0.0402       | 0.0535       | 0.0557       | 1.9631       | 0.9932       | 1.0833       | 1.0590       |
| Se$_{74}$Te$_{15}$In$_6$Pb$_5$ | 0.2342       | 0.2643       | 0.2831       | 0.2976       | 0.0629       | 0.0560       | 0.0607       | 0.0556       | 0.8484       | 1.0458       | 1.1402       | 1.2023       |
| Se$_{73}$Te$_{15}$In$_6$Pb$_6$ | 0.2365       | 0.2446       | 0.2702       | 0.2823       | 0.0335       | 0.0352       | 0.0322       | 0.0273       | 0.8359       | 0.8882       | 0.9150       | 0.8498       |
At all heating rates, ’2/3’ rule fits good for studied nano-chalcogenide materials (table 3). The deduced $T_{rg}$ values are in 2/3order, demonstrating that glass forming ability (GFA) of each investigated nano-material is high.

The distortion in local atomic configuration in amorphous chalcogenides causes changes in various kinds of photo-induced structural or photo-chemical and memory switching properties. Hence in these materials such structural transformation come from boundaries where glasses are stable; and have tendency to crystallize when heated or cooled slowly [27]. So in memory and switching materials, it is important to mention thermal stability and GFA. When physical conditions rapidly varies due to heating effect, thermal stability is an important parameter [27]. For example, In optical recording situation; amorphous state at low temperature as well as having small crystallization time. This reveals that a phenomenon of phase transformation occurring rapidly in these glassy alloys [27, 45]. Additionally, the difference among $T_p$ and $T_g$ indicates thermal stability as well as GFA of glass against crystallization. As higher values of $(T_p - T_g)$ correspond to higher thermal stability and GFA; signify a delay in nucleation procedure and kinetic resistance to crystallization. However smaller value of $(T_m - T_g)$ reveals retardation in growth procedure [32, 39]. The deduced $(T_p - T_g)$ values for all nano-crystalline system at various heating rates are tabulated in table 3. In Se-Te-In-Pb nano-chalcogenide system it is fascinating to observed that the $(T_p - T_g)$ values are maximum for Pb = 1 at. wt%. This means that glass with 1 at. wt% of Pb is thermally more stable, lesser tendency to crystallization and maximum GFA in studied system. Also Hruby [46] has given a parameter $K_{gl}$ to determine the GFA which is given as:

$$K_{gl} = \frac{K_c}{K_0} = \frac{K_c}{K_0}$$

By this relation, Hruby correlate nucleation with growth aspect of phase transformation. For investigated compositions $K_{gl}$ values at various heating rates are calculated (listed in table 4). It is stated that for $K_{gl} \leq 0.1$, a good glass forming ability has not been obtained [47]. It is clearly observed from table 4 that $K_{gl} > 0.1$, for investigated chalcogenide system; indicates good glass forming ability.

Saad and Poulain [48] have described two parameters for determining thermal stability of system, which is expressed by the following relations [32]:

$$H' = \frac{(T_o - T_g)}{T_g}$$

$$S = \frac{(T_p - T_g)}{(T_o - T_g) / T_g}$$

Thermal stability parameter illustrates resistance to devitrification after glass formation. In equation (11) rate of devitrification transformation is related to term $(T_p - T_o)$. The $H'$ and $S$ parameters are deduced (table 4). It is detected from table 4 that 1 at. wt% of Pb have highest values of $H'$ and $S$; which demonstrates that nano-
Table 5. Fragility index ($F_i$) for glassy Se$_{79}$Te$_{15}$In$_6$Pb$_1$ ($x = 0, 1, 2, 4, 6, 8$ and $10$ at. wt%) nano-crystalline composition at $5, 10, 15$ and $20$ °C min$^{-1}$ heating rates.

| Composition        | Kisssinger equation | Moynihan approximation |
|--------------------|---------------------|-------------------------|
| 5 K min$^{-1}$     | 10 K min$^{-1}$     | 15 K min$^{-1}$         | 20 K min$^{-1}$ |
| Se$_{79}$Te$_{15}$In$_6$Pb$_1$ | 33.82               | 23.19                   | 19.72           | 17.82   |
|                    | 35.07               | 24.05                   | 20.45           | 18.48   |
| Se$_{79}$Te$_{15}$In$_6$Pb$_2$ | 43.98               | 30.43                   | 25.69           | 23.21   |
|                    | 45.23               | 31.30                   | 26.43           | 23.87   |
| Se$_{79}$Te$_{15}$In$_6$Pb$_3$ | 36.30               | 25.20                   | 21.16           | 19.12   |
|                    | 37.56               | 26.07                   | 21.90           | 19.78   |
| Se$_{79}$Te$_{15}$In$_6$Pb$_4$ | 38.26               | 26.47                   | 22.35           | 20.11   |
|                    | 39.51               | 27.33                   | 23.08           | 20.76   |
| Se$_{79}$Te$_{15}$In$_6$Pb$_5$ | 14.01               | 9.40                    | 7.93            | 7.15    |
|                    | 15.28               | 10.26                   | 8.65            | 7.80    |
| Se$_{79}$Te$_{15}$In$_6$Pb$_6$ | 38.88               | 26.92                   | 22.79           | 20.43   |
|                    | 40.13               | 27.79                   | 23.47           | 21.09   |
| Se$_{79}$Te$_{15}$In$_6$Pb$_7$ | 31.44               | 21.80                   | 18.30           | 16.48   |
|                    | 32.70               | 22.68                   | 19.04           | 17.14   |

crystalline Se$_{79}$Te$_{15}$In$_6$Pb$_1$ alloy is thermally more stable than other alloys of this series. Moreover for Pb additive Se-Te-In nano-system dependence of thermal stability parameters ($T_{rg}$, $K_{gl}$, $H'$ and $S$) on heating rates are shown in figure 10, which depends on characteristic temperatures ($T_p$, $T_m$, and $T_o$). Figure 10 shows a linear dependence of $T_{rg}$, $K_{gl}$, $H'$ and $S$ on $\ln(\alpha)$, which reveals enhancement in thermal stability with heating rates.

The empirical parameters which are evaluated above have been mostly used for quantitative characterization of glass formation. As there is no standard criteria for parameterize glass formation. For measuring GFA of glassy system, fragility index ($F_i$) is a significant parameter. $F_i$ signify rate through which relaxation time reduces with temperature raising around $T_g$. $F_i$ is calculated through the following relationship [49, 50]:

$$F_i = E_g / RT_g \ln(\alpha)$$  \hspace{1cm} (12)

It is stated by Viglis that [51] glass-forming liquids that’s reveal approximate dependence on Arrhenius temperature are characterized as strong glass-forming liquids. These liquids have low value of $F_i$ ($F_i \approx 16$), whereas high value of $F_i$ ($F_i \approx 200$) signifies limit of fragile glass forming liquid [21]. Consequently in categorization of glass-formation, according to viscosities [28], it concludes that strong glass-forming liquids reveal an Arrhenius temperature dependence on viscosity. Whereas fragile glass-forming liquids show non-Arrhenius behavior. For examined compositions at various heating rates, $F_i$ is calculated by using value of $E_g$ deduced from Kissinger’s formula and Moynihan approximation and are listed in table 5. As $F_i$ values are within above-mention limit, so investigated nano Se$_{79-x}$Te$_{15}$In$_6$Pb$_x$ ($x = 0, 1, 2, 4, 6, 8, 10$) chalcogenide system are primed from strong glass-forming liquid. However, $F_i$ decreases with heating rate and this can be explained through increase in $T_g$ with heating rate.

4. Conclusions

In present research paper, the crystallization kinetics analysis has been performed for Pb additive Se-Te-In nano-chalcogenide system through DSC under non-isothermal conditions at four heating rates $5, 10, 15$ and $20$ °C min$^{-1}$. The examined nano-chalcogenide system is prepared via melt-quench process. The kinetic parameters, namely activation energy for glass transition ($E_g$), activation energy for crystallization ($E_c$), reduced glass transition temperature ($T_{rg}$), Hruby’s parameter ($K_{gl}$), thermal stability parameters ($S$ and $H'$) and fragility index ($F_i$) are derived from heating rate dependence of $T_p$ and $T_g$. It is analyzed that value of $E_g$ calculated from Moynihan’s as well as Kissinger’s approaches are consistent. The outcome shows that nano-crystalline Se$_{79}$Te$_{15}$In$_6$Pb$_1$ alloy has a higher $T_p$ value among the examined system; which indicates that this composition has maximum operation temperature, archival life time and attributes to a single phase homogeneous morphology. Also it is observed that $10$ at. wt% Pb alloy has a lower $T_{rg}$ value; which reduces the RESET current and may be useful in memory device. Additionally, the values of $E_g$ deduced by different approach are in good agreement with each other. The $K_{gl}$ is maximum for $6$ at. wt% of Pb, which indicates that Se$_{79}$Te$_{15}$In$_6$Pb$_6$ nano-crystalline system have maximum resistance to crystallization. Moreover $2/3$ rule holds good for nano-crystalline Se-Te-In-Pb chalcogenide system; signifies good glass forming ability of investigated systems. Also ($T_p$–$T_g$) is maximum for Pb = 1 at. wt% ; illustrating maximum thermal stability in analyzed compositions. $K_{gl}$, $S$ and $H'$ are also maximum for 1 at. wt% of Pb. Consequently, the deduced result shows that nano-
crystalline Se$_{78}$Te$_{15}$In$_{6}$Pb$_{1}$ system has better glass-forming ability than other composition under examination. Moreover the value of $F_i$ indicates that investigated system is obtained from strong glass forming liquids.

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