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Thermodynamic, kinetic and electrical switching studies on $Si_{15}Te_{85-x}In_x$ glasses: Observation of Boolchand intermediate phase

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ABSTRACT

An interesting topic for quite some time is an intermediate phase observed in chalcogenide glasses, which is related to network connectivity and rigidity. This phenomenon is exhibited by Si–Te–In glasses also. It has been addressed here by carrying out detailed thermal investigations by using Alternating Differential Scanning Calorimetry technique. An effort has also been made to determine the stability of these glasses using the data obtained from different thermodynamic quantities and crystallization kinetics of these glasses. Electrical switching behavior by recording I–V characteristics and variation of switching voltages with indium composition have been studied in these glasses for phase change memory applications.

1. Introduction

Amorphous chalcogenides exhibit intriguing physical properties that are not observed in their crystalline counterparts. Some of these unusual properties are extensively used in electronic and photonic devices [1], due to which there has been an intense research activity on these glasses [2–6]. Non-volatile random access memories (NVRAMs) based on chalcogenide glasses, known as phase change memories (PCMs), have become a reality in the recent times [7]. These data storage devices make use of the phenomenon of "switching" exhibited by glassy chalcogenides induced by an electric field, light or both [8–10]. The phenomenon of electrical switching in chalcogenide glasses was first observed by Ovshinsky nearly four decades ago [11]. Chalcogenide switching glasses are normally classified into two groups, namely threshold (mono-stable) or memory (bi-stable) devices depending on the type of switching exhibited (reversible or irreversible, respectively). Electrical switching in both the type of materials occurs when an appropriate voltage, known as the threshold or switching voltage (V_T), is applied and the glass switches to a high conducting ON state from a low conducting OFF state. Upon the removal of the switching field, threshold switching glasses revert back to the OFF state, whereas memory switches remain locked to the ON state. The electrical switching in both threshold and memory glasses is primarily electronic in nature and it occurs when the charged defect states in the material are filled by the field-injected charge carriers. However, additional thermal effects come into play in memory glasses which lead to the formation of a conducting crystalline channel in the electrode region [12]. Generally, glasses which are stable against devitrification exhibit threshold behavior over a large range of ON-state currents. On the other hand, glasses which are prone to easy devitrification exhibit memory switching. Phase change memories make use of chalcogenide glasses of memory switching type. On the other hand threshold switching type materials, which are thermally more stable, are having equal importance in memory device fabrication. Studies on the electrical switching behavior of chalcogenide glasses help us in identifying suitable glasses for phase change memories. The glass transition temperature (T_g) is one of the important parameters for the characterization of the glassy state in chalcogenides. In addition, a precise knowledge of the thermal crystallization kinetics is necessary for the development of suitable phase-change, erasable electrical/optical storage media. Recently, substantial efforts have been made to improve the technique of Differential Scanning Calorimetry (DSC), used widely to measure latent-heats and transformation temperatures of various thermal transitions [13]. These efforts led to evolution of a new technique, known as the Modulated or Alternating Differential Scanning Calorimetry (MDSC or ADSC), in which a sinusoidal variation is superposed on the conventional linear-ramp of temperature of DSC [14–20]. The benefits of the MDSC/ADSC technique, include the separation of the total heat flow into thermally reversing and non-reversing components, reversing heat flow (RHF) and non-reversing heat flow (NHF), respectively, from which one can measure non-reversing enthalpy change (ΔH_{NR}) and heat capacity (C_p) in a

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single experiment with increased sensitivity even for a weak thermal transition. In literature, germanium-telluride glasses belonging to the IV–VI group, have received considerable attention due to their technological applications including phase change memories [21–24]. However, comparatively fewer reports are available in literature on silicon telluride glasses, which are an efficient acoustic-optic materials and can be used as memory-type switching diodes [25,26]. Studies on various properties of silicon telluride glasses with metallic or semiconducting additives, therefore, have a particular interest. In the present work, various thermodynamic parameters such as glass transition temperature (T_g), change in enthalpy (ΔH_{NR}) during glass transition and thermal stability (ΔT) of $Si_{15}Te_{85-x}In_x$ glasses, have been studied as a function of composition ($1 \le x \le 10$). Electrical switching studies have been carried out to understand the nature of switching and also to correlate the switching voltages with activation energies for thermal crystallization calculated using Kissinger's relation. An interesting feature observed in all these investigations, is the presence of a thermally reversing window/Boolchand intermediate phase [27] in $Si_{15}Te_{85-x}In_x$ glasses. We also observed the correlation between electrical switching voltages and intermediate phase presented in non-reversing enthalpy.

2. Experimental

Bulk Si–Te–In glasses of about 1.5 g have been prepared by vacuum-sealed melt quenching method. Appropriate quantities of high purity (99.999%) constituent elements are sealed in an evacuated quartz ampoule at 10^{-5} Torr and slowly heated (approx. 100 °C/h) in a horizontal rotary furnace. The ampoules are maintained at 1100 °C and rotated continuously for about 36 h at 10 rpm to ensure homogeneity of the melt. The ampoules are subsequently quenched in a bath of ice water and NaOH mixture to get bulk glassy samples. The amorphous nature and homogeneity of the quenched samples are confirmed by X-ray diffraction technique and EDAX, respectively. Thermal analysis is carried out by ADSC (model DSC822^e, METTLER TOLEDO). ADSC scans of all samples are taken at 3 °C min^{-1} scan rate and 1 °C min^{-1} modulation rate. Various thermal parameters such as glass transition temperature (T_g), peak crystallization temperature (T_c) and non-reversing enthalpy (ΔH_{NR}) are estimated from RHF and NHF curves, which are de-convoluted from total heat flow curve obtained from ADSC scans; Fig. 1 shows the evaluation of ADSC RHF and NHF curves of a representative $Si_{15}Te_{79}In_6$ glass for various thermal parameters.

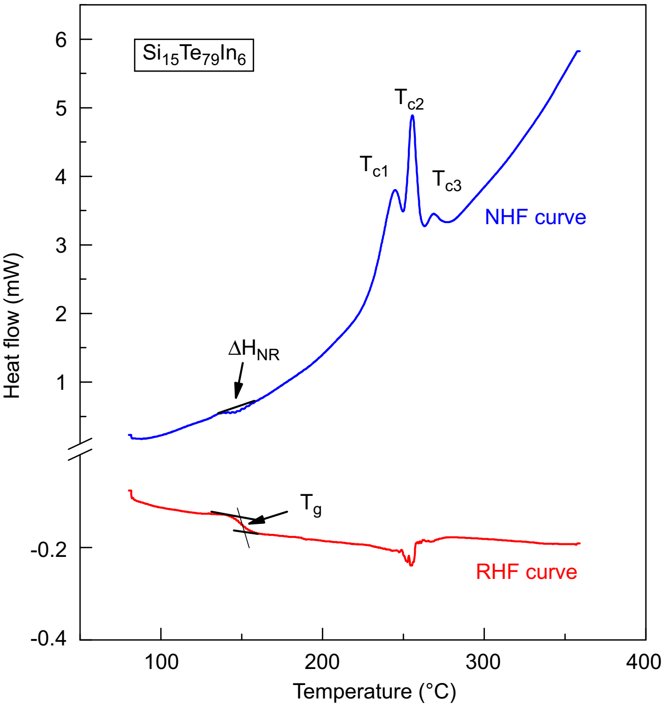

Fig. 1. Evaluation of ADSC RHF and NHF curves of a representative $Si_{15}Te_{79}In_6$ glass for various thermal parameters.

Typical error in the measurement of thermal parameters T_g and T_c is within ±1 °C. The deviations in ΔH_{NR}, measured for heating scans are found to be within ±0.05 J/g. For estimating the crystallization activation energy (E_c), DSC scans have been taken at a 5, 10, 15 and 20 °C min^{-1} scan rates in the temperature range of 80–300 °C; typical error in the measurements of crystallization temperature (T_c) is within ±2 °C. The electrical switching behavior of Si–Te–In samples are studied by recording I–V characteristics using a Keithley source-meter (Model 2410^c) controlled by LabVIEW 6i (National Instruments). The source-meter is capable of sourcing current in the range 0–20 mA at a compliance voltage of 1100 V (maximum). Samples polished to about 0.25 mm thickness are mounted between a flat-plate bottom and a point-contact top electrode made of brass. A constant current of 0–3 mA is passed through the sample and the voltage developed across the sample is measured.

3. Results and discussion

3.1. Thermal analysis and bond energy calculations

The total heat flow curves of representative $Si_{15}Te_{85-x}In_x$ glass samples ($1 \le x \le 10$), obtained using ADSC are shown in Fig. 2. It can be seen from Fig. 2 that all total heat flow curves show one endothermic glass transition peak (T_g) and three distinct exothermic crystallization peaks (T_{c1}, T_{c2} and T_{c3}). This indicates that the stable structural phases presented in Si–Te–In glasses are percolating at different temperatures. It is also observed that there is no well-defined T_{c3} for $x=1$ and $x \ge 7$; it is spread over a wide temperature range with comparatively less heat flow signal. In many of the chalcogenide systems, the coordination numbers of Si and Te obey the Mott's 8-N rule, where N is number of valance electrons [28], therefore, in the present Si–Te–In glassy system also, the coordination numbers of Si and Te can be safely assumed to be 4 and 2, respectively. Though there are no reports in literature about the coordination number of indium atoms in Si–Te–In system, it has been reported as 3.4 in the similar Ge–Te–In glassy system [29]. It is therefore assumed that in the present study that the indium atoms are 4-fold coordinated in Si–Te–In samples and also few reports available based on this assumption [30]. Using the coordination numbers 4, 2 and 4 for Si, Te and In, respectively, the average coordination ($\langle r \rangle$) for a particular composition of Si–Te–In glassy system can be calculated from the following formula [31]:

$$\langle r \rangle = \frac{r_{Si}(15)+r_{Te}(85-x)+r_{In}(x)}{100} \quad (1)$$

where r is coordination number of the respective atom.

Based on the bond energy considerations [32], the possible bonds formed in this glassy system are Si–Te, Si–Si, Te–Te, Te–In and In–In; their bonding energies (D, kJ/mol) are in the order, $D(\text{Si–Te})=429.2 > D(\text{Si–Si})=310 > D(\text{Te–Te})=257.6 \pm 4.1 > D(\text{Te–In})=215.5 \pm 14.6 > D(\text{In–In})=82 \pm 5.7$. The formation of the structural network in chalcogenide glasses can be explained by the chemical bond approach as suggested by Bicerano and Ovshinsky [33]. Accordingly, in a glassy network, bonds are formed in the sequence of decreasing bond energies until all the available valencies are saturated. Also, atoms combine more favorably with atoms of different kind than with the same kind, assuming the

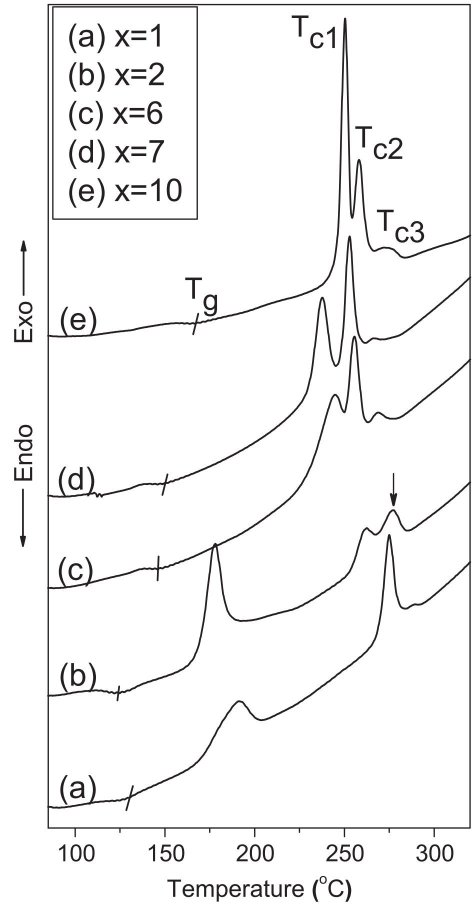

Fig. 2. The ADSC total heat flow curves of $Si_{15}Te_{85-x}In_x$ glasses with different indium concentrations (x).

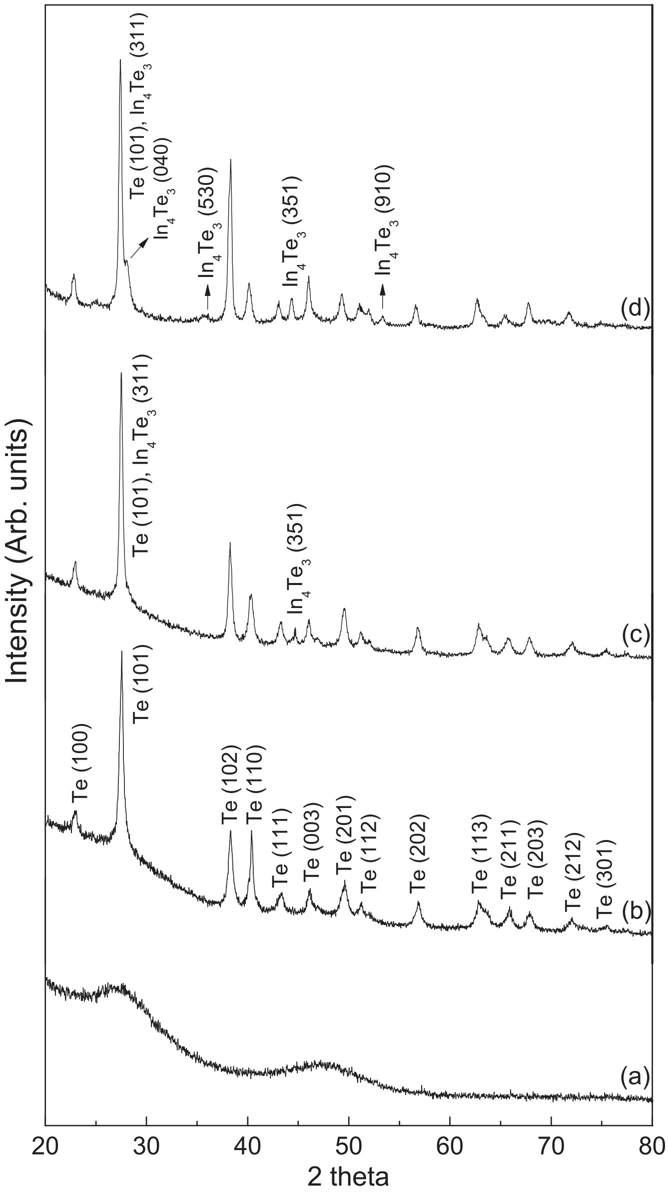

Fig. 3. The XRD patterns of (a) as prepared $Si_{15}Te_{84}In_1$ glass, showing amorphous nature; (b) $Si_{15}Te_{83}In_2$ sample at T_{c1}, showing hexagonal-Te crystalline phase; (c) and (d) $Si_{15}Te_{79}In_6$ sample at T_{c2} and T_{c3}, respectively, orthorhombic-In_4Te_3 phase in different orientations can be seen.

maximum amount of chemical ordering possible. In the $Si_{15}Te_{85}$ base glass composition, the entire four-fold coordinated Si atoms bond with two-fold coordinated Te atoms as the Si–Te bond energy is higher and the glassy network is primarily constituted by the Si–Te linkages. The Te atoms remaining after the formation of Si–Te bonds form a network among themselves. This conjecture has been earlier confirmed by the crystallization studies on $Si_{20}Te_{80}$ glasses [34], which reveal the formation of Te and $SiTe_2$ crystalline phases upon thermal devitrification. Further, the addition of 4-fold coordinated indium atoms to $Si_{15}Te_{85}$ network, at the cost of Te atoms, leads to the modification of the network, as indium atoms can bond with Te atoms as well as the Si–Te back-bone. Interestingly, in all ternary Si–Te–In glasses there is no trace of stable $SiTe_2$ phase percolation. This aspect is evident from the X-ray diffraction (XRD) pattern of crystallized Si–Te–In samples shown in Fig. 3, which reveals that the phases that crystallize out at T_{c1}, T_{c2} and T_{c3} are: hexagonal-Te with a unit cell define by $a=4.458$ Å, $c=5.925$ Å; orthorhombic-In_4Te_3 in (311) and (351) planes and orthorhombic-In_4Te_3 in (311), (040), (530), (351) and (910) planes with a unit cell define by $a=15.549$ Å, $b=12.7$ Å and $c=4.460$ Å, respectively. The variation of T_g with composition of $Si_{15}Te_{85-x}In_x$ glasses (shown in Fig. 4) indicates that there is an initial decrement in T_g in the composition range $x \leq 2$, which is followed by a continuous increase. It is known that the composition dependence of T_g of network glasses has an intimate relation with the evolution of network connectivity. An increase in T_g generally implies an increase in network connectivity [35] and a saturation/decrease in T_g is attributed to the phase separation caused by the segregation of homopolar bonds [36]. The initial decrease in T_g of $Si_{15}Te_{85-x}In_x$ glasses in the composition range $1 \leq x \leq 2$, can be due to the segregation of Te–Te homopolar bonds in Si–Te–In network. Beyond $x=2$, the addition of indium atoms affects the Te–Te network in a significant manner to develop the In–Te network. It is also interesting to note here that the first crystallization temperature T_{c1} of $Si_{15}Te_{85-x}In_x$ glasses increases with the indium addition in the region $2 < x \leq 6$ and saturates subsequently (Fig. 5). However, there is not much change in T_{c2} and T_{c3} with indium addition. It can also seen from Fig. 4 that the thermal stability and the glass forming ability (GFA) of the glass, which is directly proportional to the separation between T_{c1} and T_g ($\Delta T = T_{c1} - T_g$), increases with indium concentration in the composition range $2 < x \leq 6$. These results strongly support the idea that network connectivity and consequently the network rigidity of $Si_{15}Te_{85-x}In_x$ glasses increase in the composition region $2 < x \leq 6$. Fig. 6 shows the variation in the number of Si–Te, Te–Te and In–Te bonds, average bond energy and total bond energy (inset in Fig. 6) with indium addition. The number of bonds has been calculated using the bond formation

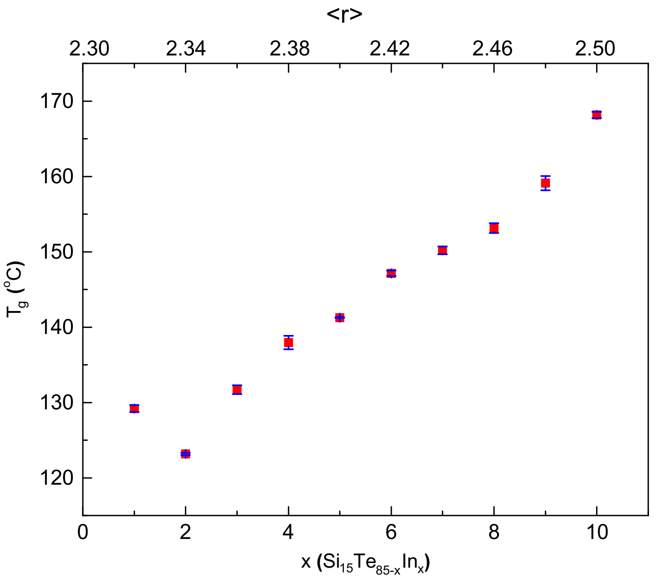

Fig. 4. The variation of glass transition temperature (T_g) of $Si_{15}Te_{85-x}In_x$ glasses with indium concentration (x) and average coordination number ($\langle r\rangle$).

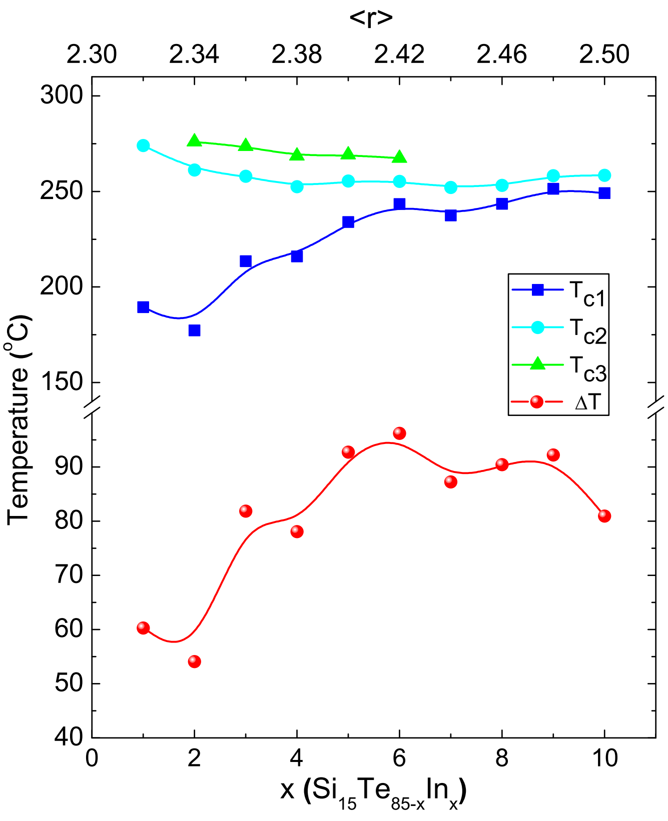

Fig. 5. The compositional dependence of T_c and $\Delta T = T_{c1} - T_g$ of $Si_{15}Te_{85-x}In_x$ glasses.

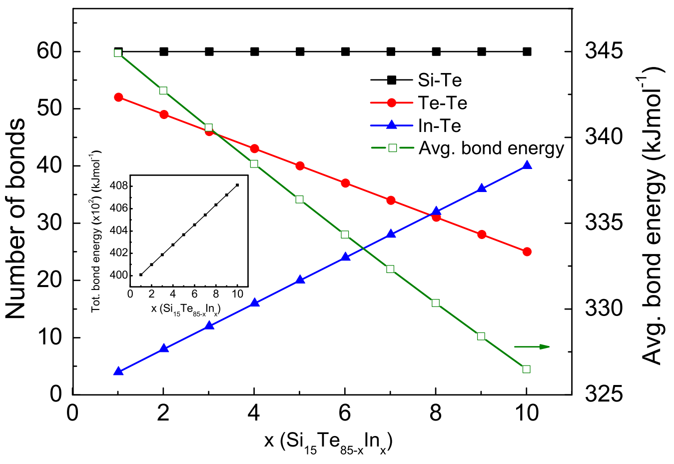

Fig. 6. The variation of number of bonds, average bond energy and total bond energy (inset) of $Si_{15}Te_{85-x}In_x$ glasses with indium composition (x).

rules and the total and average bond energies are calculated using the bond energy values. It can be seen from Fig. 6 that with indium addition, there is no change in Si–Te bond number, whereas the number of Te–Te bonds decreases and the number of In–Te bonds increases; further, the average bond energy is found to decrease with indium addition due to which a decrement in T_g and T_c can be expected. However, there is no such decrement in T_g and T_c values seen in $Si_{15}Te_{85-x}In_x$ glasses. This observed composition dependence of T_g may be because of the influence of network rigidity; with the progressive replacement of 2-fold coordinated tellurium atoms by the 4-fold coordinated indium atoms, there is a continuous change in 1-d distorted Te-chain to a rigid 3-d network [37] which increases the total number of bonds in glassy system. In this context, it is interesting to note from the inset in Fig. 6 that the total bond energy of the $Si_{15}Te_{85-x}In_x$ glassy system increases with indium addition which results in increasing T_g and T_c values.

3.2. *Relaxation enthalpy in the glass transition region*

The effect of network connectivity and rigidity on the properties of chalcogenide glasses, particularly the thermal properties, has been an interesting topic for over two decades now [35,38]. In covalently bonded glassy networks constrained by bond-stretching and bond-bending forces, a mechanical critical point is reached at an average coordination number $\langle r\rangle = 2.40$, when the number of constraints per atom equals the number of degrees of freedom of the network [39–41]. At $\langle r\rangle = 2.40$, the system undergoes a percolative transition from a floppy polymeric glass to a rigid amorphous solid. It is also shown that in certain glassy systems [42–44], the rigidity percolation transition can occur over an extended composition range, with the samples exhibiting two “stiffness transitions”, going from a floppy polymeric phase to an isostatically rigid phase and from an isostatically rigid to a stressed rigid phase. This composition range corresponding to the intermediate isostatically rigid phase constitutes the “thermally reversing window” in these systems. Various theoretical calculations based on techniques like the graph theory, constraint counting and cluster approximations have shown the existence of this intermediate phase, now known as the Boolchand intermediate phase, in several chalcogenide glassy networks [26]. The non-reversing enthalpy (ΔH_{NR}) gives the latent heat between the glass and its melt, and is used as a measure of the enthalpy involved in the relaxation of the glass structure in the glass transition region. Further, the compositional variation of ΔH_{NR} is indicative of how different a glass is from the liquid in a configurational sense. For glass compositions in the intermediate phase, the ΔH_{NR} has been found to nearly vanish [45–47], which suggests that the glass and the liquid structures in the thermally reversing window are close to each other and both are stress-free in a global sense. The most interesting result of the present thermal investigations is the variation of the non-reversing heat flow (ΔH_{NR}) with composition (x)/average coordination number ($\langle r\rangle$), shown in Fig. 7, which indicates that there is not much change in ΔH_{NR} in the composition range $1 \le x \le 2$. A decrease is seen in ΔH_{NR} above $x = 2$,

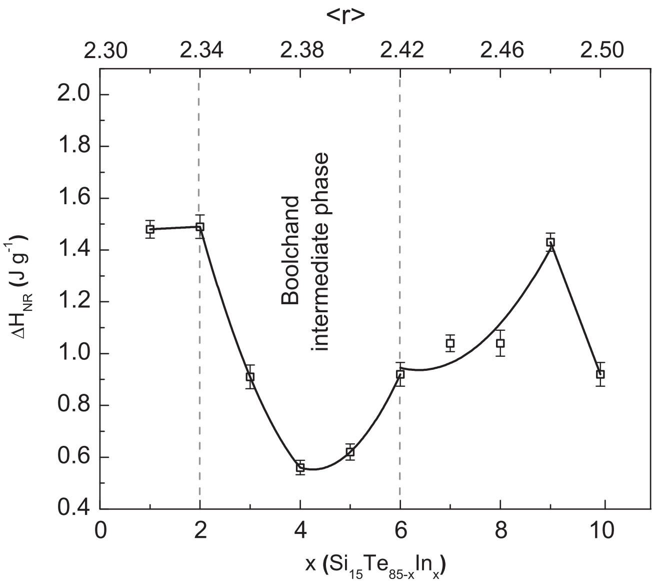

Fig. 7. The variation of non-reversing heat flow (ΔH_{NR}) of $Si_{15}Te_{85-x}In_x$ glasses with composition (x) and average coordination number ($\langle r \rangle$).

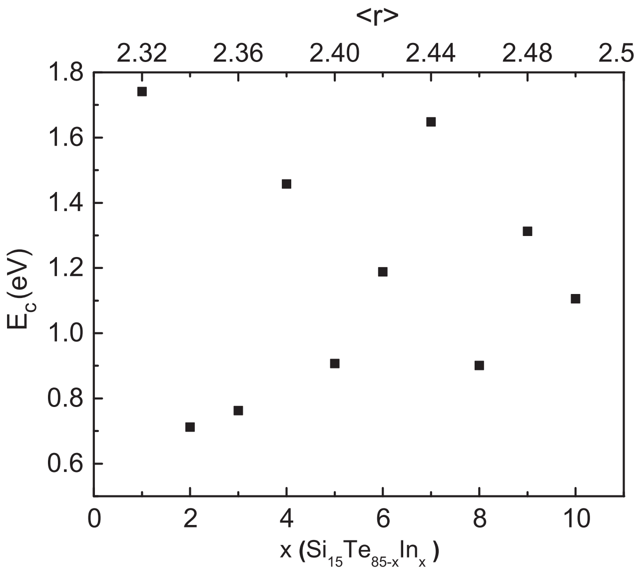

Fig. 9. The composition dependence of crystallization activation energy (E_c) of $Si_{15}Te_{85-x}In_x$ glasses.

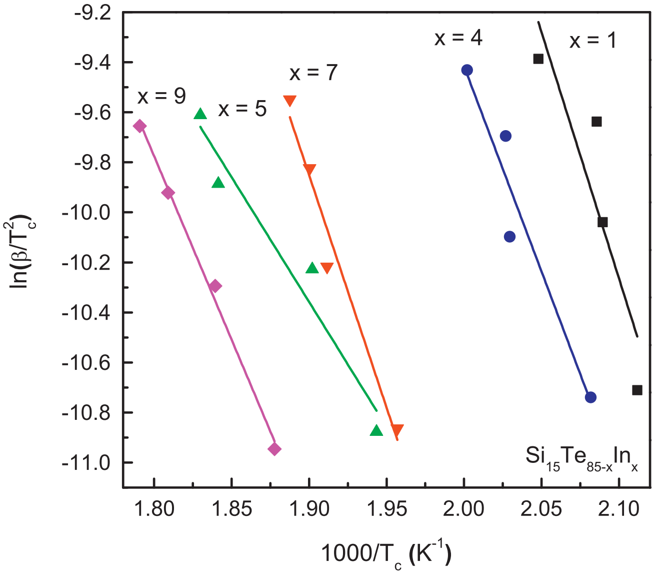

Fig. 8. Kissinger's plot of selected $Si_{15}Te_{85-x}In_x$ glassy samples; the crystallization temperatures for each sample at different scan rates are straight-line fitted.

which leads to a trough in the composition range $2 < x \leq 6$ ($2.34 < \langle r \rangle \leq 2.42$), which clearly indicates the presence of a thermally reversing window in this composition range.

3.3. Crystallization kinetics

The crystallization activation energy (E_c) of bulk $Si_{15}Te_{85-x}In_x$ ($1 \leq x \leq 10$) glasses are calculated using Kissinger's relation. The values of *only first crystallization peak temperature* ($T_{c1} = T_c$) are taken for activation energy calculations. According to Kissinger [48], the crystallization temperature (T_c) and heating rate (β) can be expressed as:

$$\ln\left(\frac{\beta}{T_c^2}\right) = -\frac{E_c}{RT_c} + \text{const.} \tag{2}$$

Fig. 8 shows $\ln(\beta/T_c^2)$ vs. $1/T_c$ plots of selected $Si_{15}Te_{85-x}In_x$ glasses. Eq. (2) is used to calculate the activation energies by measuring corresponding linear fit plots slope. Fig. 9 shows the variation of average crystallization activation energy (E_c) with indium composition (x). It can be observed from Fig. 9 that E_c span wide range of values from 0.70 eV to 1.75 eV and several local maxima and minima observed at different indium compositions. It is known that the activation energy of crystallization is associated with the nucleation and growth processes that dominate the devitrification in most of the glassy solids [49,50]. Recent studies on crystallization kinetics of Se–Te–Ag alloys [51] reveal non-systematic activation energy values which has been understood on the basis of atomic weights of Te and Ag; a decrease in mean atomic weight of the ternary alloy leads to an increase in the nucleation and growth rate. In the present $Si_{15}Te_{85-x}In_x$ system studied, no such clear relation can be established even though the mean atomic weight decreases with indium addition. In this case, it is likely that the network connectivity and the number of stable crystallization phases present, particularly in multi stable phase percolated glasses, also play major role in thermal activation energies.

3.4. Electrical switching behavior

The current–voltage (I–V) characteristics of selected glasses, representing the $Si_{15}Te_{85-x}In_x$ series, obtained using a current sweep, are shown in Fig. 10. It can be seen that these glasses switch from a high resistance OFF to a low resistance ON state at a threshold voltage V_T (corresponding to a threshold current I_T); upon reducing the current in the ON state (at currents less than 3 mA), all the $Si_{15}Te_{85-x}In_x$ samples studied (except $Si_{15}Te_{83}In_2$), revert back to the high-resistance state. This indicates that these glassy samples exhibit threshold switching behavior; however $Si_{15}Te_{83}In_2$ sample exhibits the memory switching behavior. There are several factors which decide whether a chalcogenide glass will exhibit memory or threshold type electrical switching:

The ON state current: This is one of the trivial factors, which decides whether a sample will exhibit threshold or memory behavior. If the current flowing through the conducting channel is limited below a certain value (which is different for different glassy systems), the threshold behavior is seen. However, memory behavior may be exhibited at higher ON state currents due to larger Joule heating.

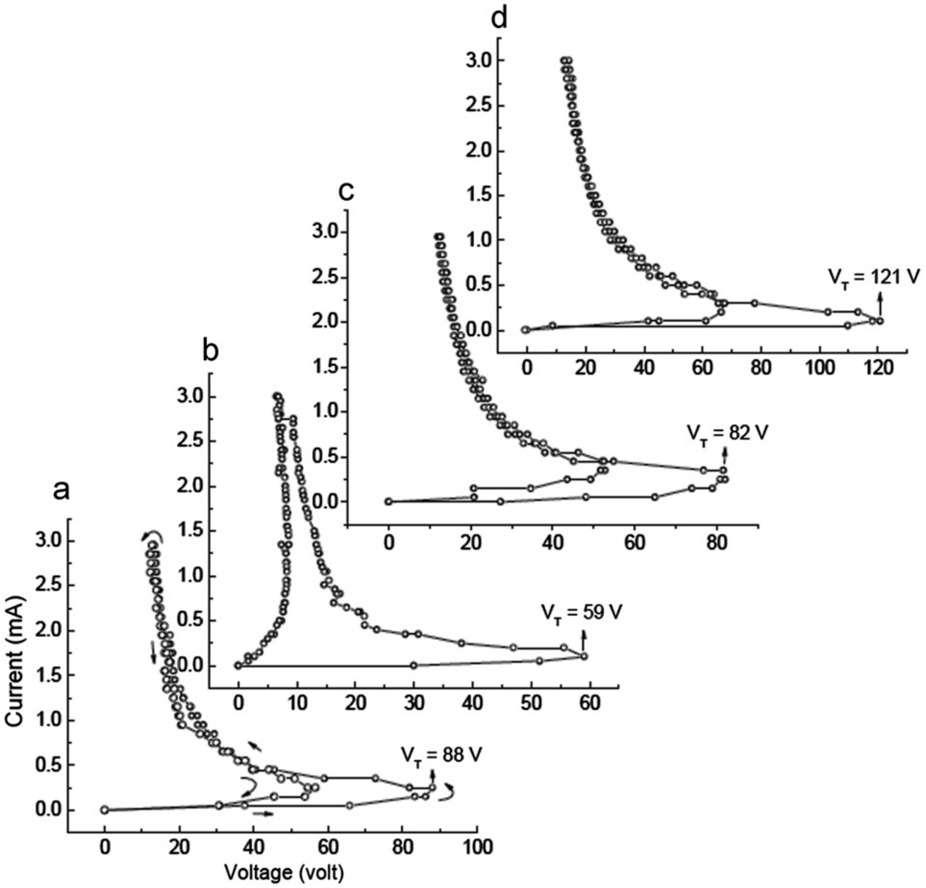

Fig. 10. The current–voltage characteristics of selected $Si_{15}Te_{85-x}In_x$ glasses. (a) $x=1$; (b) $x=2$; (c) $x=5$; (d) $x=10$.

The thermal stability: Glasses which are thermally less stable which are prone to easy devitrification are generally expected to show the memory behavior even at lower ON state currents. The thermal stability of a glass is usually quantified by two independent factors, namely $\Delta T = T_c - T_g$ and the enthalpy released during crystallization. The activation energy for crystallization (E_c) is another thermal parameter which determines the stability of a glass against devitrification.

Thermal diffusivity: The temperature rise in the conducting filament is primarily decided by the rate at which heat is dissipated away from the electrode region to the bulk of the material, which in turn is decided by the thermal diffusivity of the glass. Memory switching is more probable in glasses with lower thermal diffusivity, compared to those with higher thermal diffusivity.

Network topological effects: The network connectivity and rigidity (which are determined by the coordination numbers of the constituents) have been found to play a crucial role in the electrical switching behavior of glassy chalcogenides. Generally, memory switching is observed in elastically floppy glasses, with poor network connectivity, which are easily devitrifiable.

The present results indicate that with composition, $Si_{15}Te_{85-x}In_x$ glasses show a change in the switching behavior, namely from threshold ($x=1$) to memory ($x=2$) to threshold ($x>2$). From the network connectivity point of view, no change in the switching behavior of the $Si_{15}Te_{85-x}In_x$ system is expected with composition, as the network connectivity and rigidity is expected to have a continuous evolution, with the addition of 4-fold coordinated indium atoms. However, the glass transition temperature of $Si_{15}Te_{85-x}In_x$ glasses shows an initial decrease ($x=2$) and a subsequent increase with indium addition ($x>2$) (Fig. 4). As mentioned earlier, an increase in T_g generally implies an increase in network connectivity [35], whereas a saturation/decrease in T_g is attributed to the phase separation caused by the segregation of homopolar bonds [36]. At first sight, the memory behavior seen in $Si_{15}Te_{83}In_2$ sample may be associated with the same effect which causes an initial decrease in T_g. The memory switching behavior exhibited by $Si_{15}Te_{83}In_2$ sample seems to be more directly connected with the composition dependence of thermal stability of $Si_{15}Te_{85-x}In_x$ glasses. The present thermal studies indicate that there is an initial decrease in the thermal stability ΔT (Fig. 5) of $Si_{15}Te_{85-x}In_x$ glasses with the indium addition ($x \leq 2$); the memory switching exhibited by the $Si_{15}Te_{83}In_2$ sample is due to this initial decrease in ΔT. The subsequent increase in ΔT of $Si_{15}Te_{85-x}In_x$ glasses ($x>2$) is consistent with the threshold switching nature exhibited by these samples. Fig. 11 shows the variation of the threshold voltages of $Si_{15}Te_{85-x}In_x$ glasses with indium addition. It can be seen that V_T decreases initially with an increases in indium concentration, exhibiting a minimum at $x=4$ ($\langle r \rangle = 2.38$). A gradual increment is seen in V_T above 4% of In. It is also seen from Fig. 11 that the local minimum at $x=2$. However, this value cannot be compared with other V_T values because of memory switching nature and switching voltages vary depending on the switching nature of the sample. The resistivity of the dopant atom and the network connectivity are the two dominant factors which determine the variation of switching voltages of chalcogenide glasses, as a function of composition. The addition of metallic dopants tends to decrease the resistivity of the material and in turn the switching voltage. On the contrary, the increase in network connectivity and network rigidity lead to an increase in switching voltage [52]. The present results indicate that both the effect of metallicity of

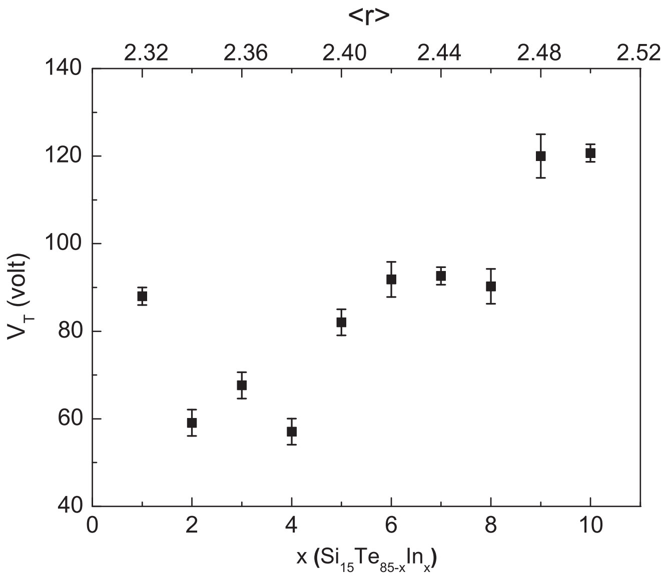

Fig. 11. The variation of switching voltages (V_T) of $Si_{15}Te_{85-x}In_x$ glasses ($1 \le x \le 10$), of different indium compositions.

the dopant and the influence of network connectivity and rigidity are seen on the composition dependence of V_T of $Si_{15}Te_{85-x}In_x$ glasses. Based on the metallicity factor, the switching voltages of $Si_{15}Te_{85-x}In_x$ glasses is expected to decrease with addition of In. At the same time an increase in network connectivity and rigidity, due to the addition of higher coordinated indium atoms, is expected to lead to an increase in switching voltage of $Si_{15}Te_{85-x}In_x$ glasses. The migration of In^+ ions also plays a crucial role in the switching behavior of Si–Te–In glasses. In the OFF state, the following recombination processes dominate: the hole capture by C_1^-centers ($C_1^- + e^+ \rightarrow C_1^0$) and the electron capture by C_3^+ centers ($C_3^+ + e^- \rightarrow C_3^0$). The In^+ ions present in the sample can be involved in the passivation of C_1^- centers through diffusion [53], thereby reducing the voltage required to initiate the switching effect and also the time taken to switch the sample. The initial decrease in V_T of $Si_{15}Te_{85-x}In_x$ glasses is due to the metallicity factor and faster passivation of charged defect states and the subsequent increase is due to the network effect. It is interesting to note from the present results that there is a broad trough seen in the composition dependence of switching voltages in the composition range $1 \le x \le 6$ (this could also be in the range $2 \le x \le 6$—we could not find exact range due to memory switching nature of $Si_{15}Te_{83}In_2$ glass), which is also the region where thermally reversing window observed from the compositional variation of ΔH_{NR}. The present $Si_{15}Te_{85-x}In_x$ glassy system is one of the few glassy systems in which the thermally reversing window is seen in the composition dependence of switching voltages. It is also seen from the present results that there is no correlation between the composition dependences of non-reversing heat flow/switching voltages and activation energies of crystallization of $Si_{15}Te_{85-x}In_x$ glasses. The reason for this being the correlation between the switching voltages and crystallization activation energies is more direct in memory switching glasses [54] and the present $Si_{15}Te_{85-x}In_x$ samples are mostly threshold switching in nature.

4. Conclusions

ADSC studies on $Si_{15}Te_{85-x}In_x$ ($1 \le x \le 10$) glasses indicate that these samples show one endothermic glass transition peak (T_g) and three distinct exothermic crystallization peaks indicating that these glasses comprises of different stable phases percolating at different crystallization temperatures. The composition dependence of glass transition and first crystallization temperatures of $Si_{15}Te_{85-x}In_x$ glasses show that there is an initial decrement in the composition $x \le 2$, which is followed by a continuous increase in the region $2 < x \le 6$. Also, the $Si_{15}Te_{85-x}In_x$ glasses, in the composition range $2 < x \le 6$, are found to exhibit high thermal stability. The average bond energy of $Si_{15}Te_{85-x}In_x$ glasses decreases with composition, whereas the total bond energy of the system increases. The non-reversing heat flow (ΔH_{NR}) has been found to exhibit a trough between the compositions $x=2$ and 6 ($\langle r \rangle = 2.34$ and 2.42), which clearly indicates the presence of a Boolchand intermediate phase in $Si_{15}Te_{85-x}In_x$ glasses. It is interesting to note that the crystallization activation energy, E_c, of $Si_{15}Te_{85-x}In_x$ glasses, which span a wide range from 0.70 eV to 1.75 eV, exhibit no systematic change with indium addition. Electrical switching studies indicate that all the $Si_{15}Te_{85-x}In_x$ samples studied except $Si_{15}Te_{83}In_2$, exhibit threshold switching behavior; $Si_{15}Te_{83}In_2$ sample is found to exhibit memory type electrical switching. The change in the switching behavior of $Si_{15}Te_{85-x}In_x$ glasses, namely from threshold ($x=1$) to memory ($x=2$) to threshold ($x > 2$), seems to be connected with the decrease in T_g and thermal stability with indium addition. The lowest activation energy for crystallization is also consistent with the memory switching exhibited by $Si_{15}Te_{83}In_2$ sample. Further, the switching voltages (V_T) of $Si_{15}Te_{85-x}In_x$ glasses is found to initially decrease with indium addition exhibiting a broad trough in the composition range $2 \le x \le 6$, the thermally reversing window deciphered from the variation with composition of ΔH_{NR}. It is also found that there is no correlation seen between the switching voltages and activation energies of crystallization of $Si_{15}Te_{85-x}In_x$ glasses.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.10.034.

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