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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 ($\Delta H_{NR}$) 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 ($\Delta H_{NR}$) during glass transition and thermal stability ($\Delta T$) of $Si_{15}Te_{85-x}In_x$ glasses, have been studied as a function of composition ($1 \leq x \leq 10$). 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 ($\Delta H_{NR}$) 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.

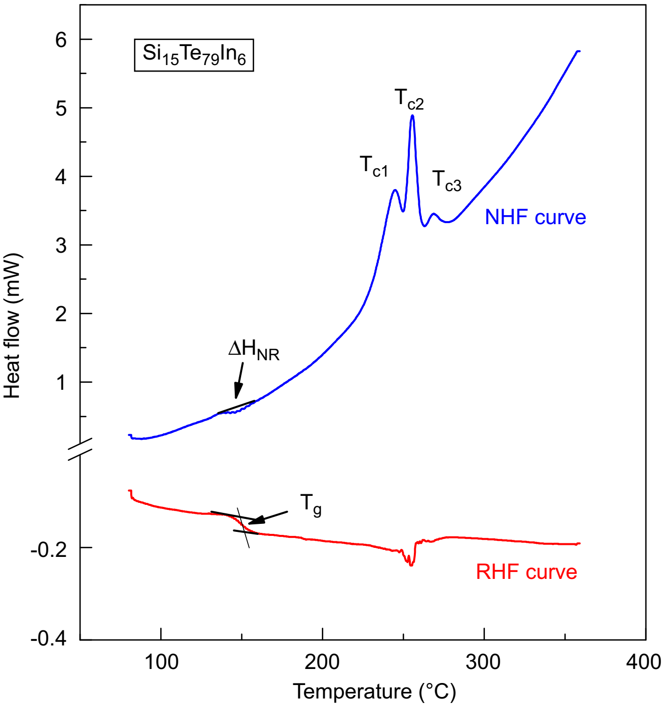

**Fig. 1.** Evaluation of ADSC RHF and NHF curves of a representative $Si_{15}Te_{79}In_6$ glass for various thermal parameters.

Typical error in the measurement of thermal parameters $T_g$ and $T_c$ is within ±1 °C. The deviations in $\Delta H_{NR}$, 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 ($1 \leq x \leq 10$), 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 $x \geq 7$; 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]:

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

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, $D$(Si–Te)=429.2 > $D$(Si–Si)=310 > $D$(Te–Te)=257.6±4.1 > $D$(Te–In)=215.5±14.6 > $D$(In–In)=82±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