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Observation of a thermally reversing window in bulk $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses

N Manikandan and S Asokan¹

Department of Instrumentation, Indian Institute of Science, Bangalore 560012, India

E-mail: sasokan@isu.iisc.ernet.in

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Abstract

Alternating differential scanning calorimetry measurements have been undertaken on the $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) series of glasses. It is found that there is a marginal decrease in the glass transition temperature (T_g) in the composition range $1 \leq x \leq 3$. Above $x = 3$, a monotonic increase is seen in T_g which indicates a continuous build-up in network connectivity and absence of any nanophase separation. The non-reversing heat flow (ΔH_{NR}) has been found to exhibit a broad trough between the compositions $x = 3$ and 7, which clearly indicates the presence of a thermally reversing window in $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses in the composition range $3 \leq x \leq 7$.

X-ray diffraction studies on crystallized Ge–Te–In samples reveal the presence of hexagonal Te, rhombohedral GeTe and monoclinic In_2Te_5 phases. An increase is observed in the intensity of the In_2Te_5 peaks as a function of indium concentration.

1. Introduction

Temperature-modulated differential scanning calorimetry (TMDSC) is one of the most sensitive techniques used in recent years for the identification of various thermal parameters in network glasses [1–3]. This technique offers the possibility of de-convoluting the total heat flow curve into reversing and non-reversing component. The extraction of the reversing and non-reversing heat flow components of the total heat flow makes possible the separation of overlapping thermal phenomena such as crystallization and glass transition. Also, in MDSC, the heat capacity can be measured directly with high accuracy from a single run, whereas in conventional DSC multiple runs are required. Further, TMDSC gives a measure of the non-reversing enthalpy, the composition dependence of which provides information about the presence a thermally reversing window in the glassy system [4–8].

¹ Author to whom any correspondence should be addressed.

It has been realized recently that the phase change memories based on chalcogenide glasses can be a replacement for conventional flash non-volatile random access memories (NVRAMs) [9–11]. The basic principle of operation of chalcogenide phase change memory is ‘electrical switching’, which is electrothermal in nature [12–14]. A close correlation has been observed between the thermal parameters and electrical switching behavior in several chalcogenide glassy systems [15–17]. Studies on the thermal behavior and the composition dependence of thermal parameters are therefore important for identifying suitable glass compositions for phase change memory applications.

This paper reports thermal studies on $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) series of glasses undertaken using temperature-modulated alternating differential scanning calorimetry (ADSC, an equivalent of MDSC). The main aim of this study is to understand the thermal behavior of these glasses and also to explore the possibility of occurrence of a thermally reversing window in this system.

2. Experiment

Bulk $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) glasses have been prepared by the melt-quenching method. Pure elements of Ge, Te and In were weighed and sealed in a quartz ampoule under a vacuum of 10^{-5} Torr. The samples were heated in a rotating furnace to 950°C and maintained at this temperature for about 24 h. The ampoules were subsequently quenched in an ice-water + NaOH mixture. The amorphous nature of the as-quenched samples was confirmed by x-ray diffraction.

ADSC studies were carried out in a Metler Toledo differential scanning calorimeter (Model 822^e). The samples were subjected to a heating rate of 2°C min^{-1} with 1°C as the scan amplitude in the temperature range of $50\text{--}450^\circ\text{C}$. Prior to the ADSC scan, all the samples were stabilized for 5 min at a constant temperature of 75°C (which is well below the glass transition temperature), in order to maintain the same thermal history. The thermograms were deconvoluted to obtain the reversing, non-reversing and the total heat flow curves. The glass transition temperature (T_g) and the non-reversing heat flow (ΔH_{NR}) values were extracted from the reversing and the non-reversing curves respectively.

3. Results and discussion

3.1. Composition dependence of thermal parameters and the presence of extended rigidity percolation

Figure 1 shows the variation of the glass transition temperature (T_g) with composition (x)/average coordination number ($\langle r \rangle$), for $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) glasses. Here, the average coordination numbers have been calculated using the coordination number of 2 for Te and 4 for Ge and In [18, 19].

The composition dependence of the glass transition temperature of network glasses has an intimate relation with the evolution of network connectivity. An increase in the glass transition temperature implies an increase in network connectivity [20]. In many chalcogenide glassy systems, a maximum is exhibited in the glass transition temperature at a certain composition, beyond which a decreasing trend is seen in T_g values. This decrease has been attributed to the nanophase separation in these glasses caused by the segregation of homopolar bonds [21]. There have also been efforts reported in the literature to link the glass transition temperature with parameters quantifying the network connectivity such as the average coordination number ($\langle r \rangle$) [22].

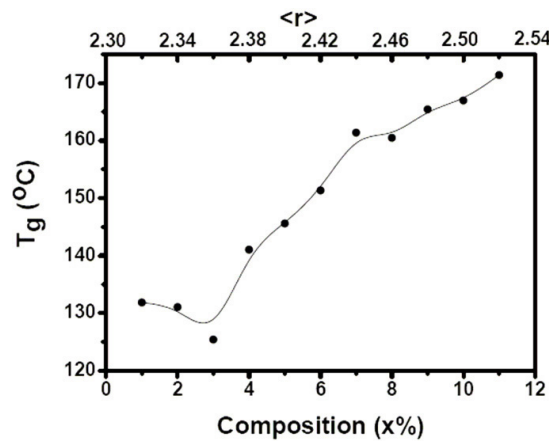


Figure 1. Variation of the glass transition temperature (T_g) with composition (x) of the $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) series of glasses.

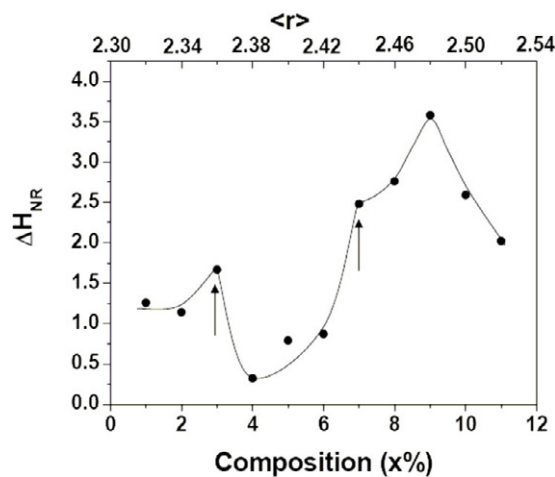


Figure 2. Variation of non-reversible heat flow (ΔH_{NR}) with composition (x) of the $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) series of glasses.

It could be observed that, in the present $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glassy system, there is not much variation in T_g in the composition range ($1 \leq x \leq 3$), which indicates that there is no appreciable change in the network connectivity in this composition range. Further, a monotonic increase in T_g is seen beyond $x = 3$ and until $x = 11$. This is suggestive of a continuous increase in network connectivity and the absence of any nanophase separation in the $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glassy system in the composition range investigated.

Figure 2 shows the variation of the non-reversing heat flow (ΔH_{NR}) with composition, which indicates that there is not much change in ΔH_{NR} also, in the composition range $1 \leq x \leq 3$. A decrease is seen in the non-reversing heat flow above $x = 3$, which leads to a broad trough in ΔH_{NR} , between the compositions $x = 3$ and 7.

The effect of network connectivity and rigidity on the properties of chalcogenide glasses has been an interesting topic for quite some time [20, 23–25]. In covalently bonded networks constrained by bond-stretching and bond-bending forces, a mechanical critical point occurs 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 [26–28]. At $\langle r \rangle = 2.40$, the system undergoes a percolative transition from a floppy polymeric glass to a rigid amorphous solid. In a few glassy systems, the rigidity percolation transition has been found to occur at higher values of $\langle r \rangle$. This shift has been attributed to other constraints acting on these systems [29–31].

In certain glassy systems, the rigidity percolation transition can occur over an extended composition range, with the samples exhibiting two 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 in glassy networks [32]. The presence of the intermediate phase has also been conclusively shown in a variety of experiments including TMDSC and Raman scattering [33–36].

The non-reversing enthalpy (ΔH_{NR}), measured in the ADSC experiments, gives the latent heat between the glass and its melt. 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} term has been found to nearly vanish [35–37], which suggests that the glass and the liquid structures in the thermally reversing window are closely similar to each other and that both are stress free in a global sense. The broad trough seen in the ΔH_{NR} of $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses between the compositions $x = 3$ and 7 clearly indicates the presence of a thermally reversing window in this composition range.

In this context it is interesting to note that the variation with composition of the electrical switching voltages and photo response of $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses also reveal the possibility of an extended rigidity percolation and a thermally reversing window in $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses in the composition range $3 \leq x \leq 7$ [38, 39].

3.2. Crystallization behavior of $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses

Based on the bond energy consideration and chemical bond arguments [40, 16], it is expected that, in $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses, the Ge–Te bonds forms the backbone of the network and the excess Te atoms will form Te–Te homopolar bonds. Above 3 atom%, the addition of four-fold coordinated indium atoms into the network results in the progressive replacement of the existing homopolar Te–Te bonds by In–Te heteropolar bonds. The heteropolar In–Te bonds are favored in accordance with the chemically ordered network model, though based on a simple bond strength approach Te–Te bonds are more favorable [41]. The replacement of homopolar Te–Te bonds with In–Te bonds leads to the network stiffening and the rigidity percolation effects as described in the previous sections.

X-ray diffraction (XRD) studies were undertaken to identify the phases which crystallize out while heating $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glasses. The samples were annealed in vacuum for 2 h at their respective crystallization temperatures and subjected to x-ray investigations. Figure 3 shows the XRD patterns of representative Ge–Te–In samples after crystallization; they can be indexed for the presence of hexagonal tellurium, rhombohedral GeTe and monoclinic In_2Te_5 phases [42]. It is also seen that Te peak dominates in most of the samples and the In_2Te_5 peak intensities increase with the increase in indium concentration.

There have been earlier studies on the thermal crystallization behavior of copper- and silver-doped Ge–Te glasses [43]. A comparison of the crystallization behavior of Ge–Te glasses with Cu, Ag and In additives indicates that indium does not behave like Cu or Ag additives in the Ge–Te matrix.

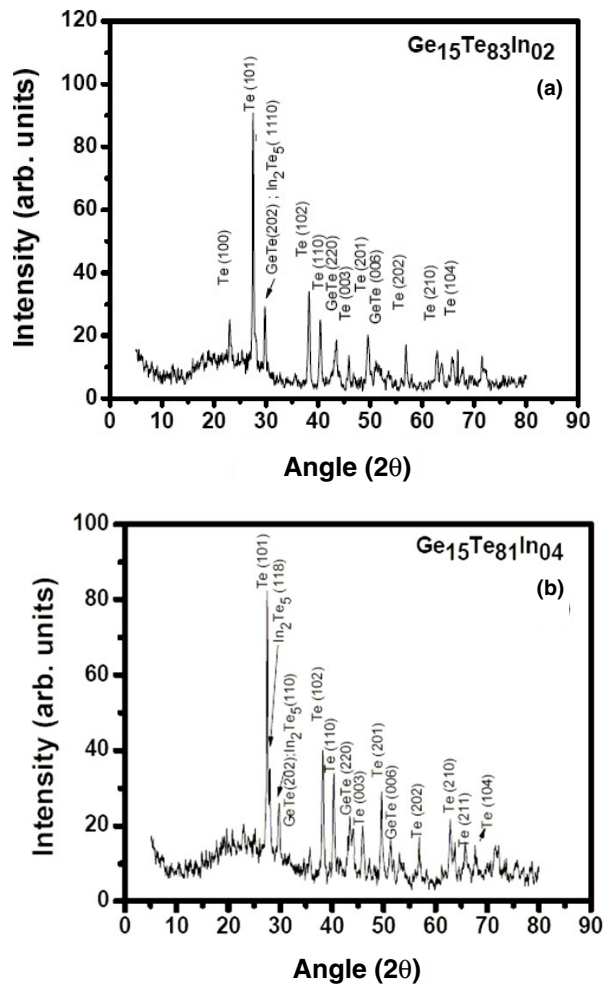


Figure 3. X-ray diffraction patterns of representative (a) $\text{Ge}_{15}\text{Te}_{83}\text{In}_{02}$ and (b) $\text{Ge}_{15}\text{Te}_{81}\text{In}_{04}$ samples after crystallization.

Copper, being similar to germanium in its electronegativity and atomic radius, undergoes a substitution reaction, thereby forming a pseudo-binary system. Hence, x-ray investigations on crystallized Cu-Ge-Te samples do not show the presence of any Cu peaks. Silver, on the other hand, forms a ternary phase in addition to the possible binary phases. In the case of indium atoms, the higher value of electronegativity and the difference in the atomic radius prohibits the formation of any Ge-In phase. Also, indium does not form any ternary phase involving Ge and Te as in the case of Ge-Te-Ag glasses. As mentioned earlier, the crystallization of Ge-Te-In samples leads to the formation of rhombohedral GeTe and monoclinic In_2Te_5 phases, with the increase in the intensity of the In_2Te_5 peaks as a function of composition.

4. Conclusions

ADSC measurements on $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ ($1 \leq x \leq 11$) glasses indicate that indium atoms up to about 3 atom% do not enter the Ge-Te network. A continuous increase is seen in T_g above

$x = 3$, which is suggestive of an increase in network connectivity and rigidity. Also, there is not much change in non-reversing heat flow (ΔH_{NR}) in the composition range $1 \leq x \leq 3$. A decrease is seen in ΔH_{NR} above $x = 3$, which leads to a broad trough between the compositions $x = 3$ and 7. Based on this, it is proposed that the $\text{Ge}_{15}\text{Te}_{85-x}\text{In}_x$ glassy system exhibits an extended rigidity percolation with a thermally reversing window in the composition range $3 \leq x \leq 7$.

X-ray diffraction studies on crystallized Ge–Te–In samples reveal the presence of hexagonal Te, rhombohedral GeTe and monoclinic In_2Te_5 phases, with the increase in the intensity of the In_2Te_5 peaks as a function of indium concentration.

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