

Effect of Thallium Addition on Thermal and Electrical Properties of Germanium Telluride Chalcogenide Glasses

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Abstract

$Ge_{17}Te_{83-x}Tl_x$; ($0 \leq x \leq 13$) glasses were prepared in melt quenching method. Electrical switching and alternating differential scanning calorimetric (ADSC) studies have been carried out to observe the effect of Thallium addition on thermal and electrical properties of these glasses. It was found that the glasses show the memory type of switching and single glass transition temperature. The switching voltage V_{th} and glass transition temperature T_g decreases with increasing thallium concentration largely in the composition range $0 \leq x \leq 6$ and much slower for $x \geq 7$.

Index Terms— Chalcogenides glasses; Electrical switching; glass transition.

1. Introduction

Amorphous materials can be electrically insulating, semiconducting or metallic in nature. Amorphous semiconductors have attracted immense interest in the field of phase change memory (PCMs) applications due to their electrical and optical properties [1-3] and are potential candidates for many commercial applications [4, 5]. Phase change memories based on chalcogenide glasses have been found to be suitable candidates for replacing the conventional flash non-volatile random access memories (NVRAMS). They exhibit two types of switching behaviour; threshold and memory switching, and this switching behaviour is central to their technological importance and their uses as memories [6]. Switching phenomenon is electro thermal in nature, and several chalcogenide glasses reveal a close relation between their thermal parameters and electrical switching. Studies on the composition dependence of electrical and thermal parameters are therefore important for identifying suitable glass compositions for phase change memory applications. That's why investigation on switching voltage V_{th} , glass transition temperature T_g , crystallization temperature T_c with the variation of an additive are essential for the selection of a promising candidate for memory applications. This paper represents the effect

of thallium addition on the switching and thermal behaviour of $Ge_{17}Te_{83-x}Tl_x$; ($0 \leq x \leq 13$) series of glasses.

2. Experimental Details

The concentration triangle as shown in figure 1 indicates the region for the amorphous phase of the Ge-Te-Tl ternary system [7] and the tie-line of $Ge_{17}Te_{83-x}Tl_x$; $0 \leq x \leq 13$ glasses studied.

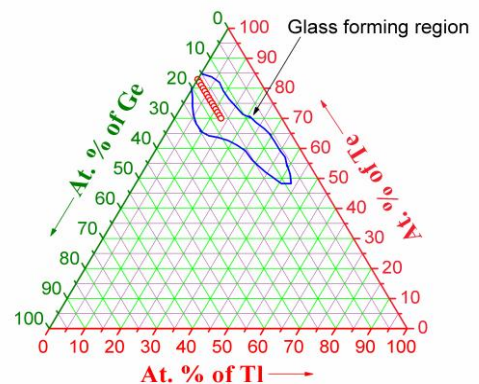


Figure-1: The phase diagram of Ge-Te-Tl ternary system shows the glass forming region and the compositions $Ge_{17}Te_{83-x}Tl_x$; ($0 \leq x \leq 13$) tie line.

As can be seen, Ge is kept fixed at 17 atomic percent and the Tl is added such that it reduces Te. If Mott 8-N rule is assumed, the coordination number of Ge, Te and Tl is 4, 2 and 3 respectively then the tie-line was chosen within the glass forming region to span the average coordination 2.4 which is likely to be the mechanical threshold. Glasses $Ge_{17}Te_{83-x}Tl_x$; ($0 \leq x \leq 13$) were prepared by standard melt quenching method. Appropriate amounts of 99.99 % pure components weighed to 0.01 mg accuracy were sealed in quartz ampoules of inner & outer diameters 5 and 7 mm respectively, under a vacuum of about 10^{-6} mbar. The ampoules were made flattened to reduce the inner radius so that the temperature gradient inside the ampoule will be negligible while quenching. Thus the cooling rate will be the same for inner part of the ampoules as the outer part. The ampoules were loaded in a horizontal rotary furnace in which the temperature

was increased step by step to a temperature above the melting point of all constituents, in Ge–Te–Tl to around 1000°C, at the rate of 100°C/hour. The ampoules were maintained at 1000°C for 24 hours with constant rotation at 10 rpm, to ensure homogeneity of the melt. The melt was subsequently quenched in a mixture of ice cold water and NaOH to get bulk glasses. X-ray diffraction on powder samples by using Philips X’pert Pro X-ray Diffractometer, PW 3050/60 (Theta/Theta) goniometer, Cu K α radiation confirmed the amorphous nature of the glasses as shown in figure 2. ADSC studies were performed using a Mettler Toledo Alternating Differential Scanning Calorimeter (Model 822e) with the aid of STAR[®] software. The switching behavior of the above samples were studied on a set up using a Keithley Source-Meter[®] (model: 2410c) unit controlled by LabVIEW 6.1 (National Instruments) software.

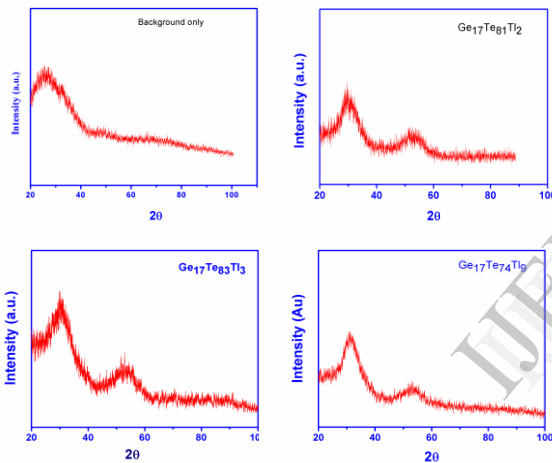


Figure-2: The XRD patterns showing the amorphous nature of as quenched representative glasses.

3. Results

Figure-3 shows the ADSC thermogram of a representative Ge₁₇Te₇₉Tl₄ glass in which the general features observed is the presence of single glass transition reaction T_g, exothermic peaks at crystallization temperatures T_{c1}, and T_{c2}. The typical error in these measurements was within ± 2 °C for T_g, and T_c

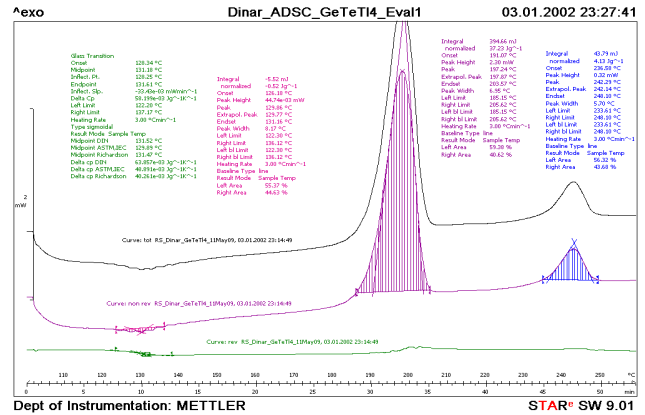


Figure-3: ADSC thermogram of a representative Ge₁₇Te₇₉Tl₄ glass which indicates the presence of T_g, T_{c1} and T_{c2}.

Figure-4 shows the variation of T_g with the atomic percent x of thallium in the series Ge₁₇Te_{83-x}Tl_x, (0 ≤ x ≤ 13) glasses. It is seen that the glass transition temperature decreases continuously up to 6 atomic percent of thallium with a little fluctuation at x=3 and is more or less constant between 6 and 12 atomic percent of thallium. A step increase is seen in T_g at the composition Ge₁₇Te₇₀Tl₁₃.

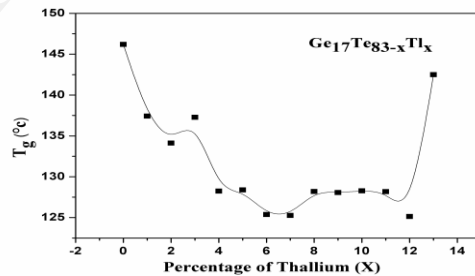


Figure-4. Variation of glass transition temperature T_g with thallium percentage X.

Figure-5 shows the variation of electrical switching voltage V_{th} as a function of atomic percent of thallium in which a large decrease in V_{th} up to x=6 and then a much slower decrease for 7 ≤ x ≤ 12 is observed [8].

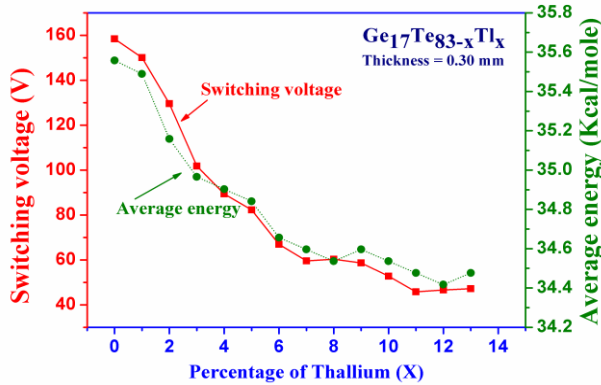


Figure-5: The variation of switching voltage and the corresponding average bond energy with Thallium percentage.

4. Discussion

The decrease in T_g and V_{th} can be attributed to the increased metallicity of thallium ($\rho_{Te}=10 \times 10^{-5} \Omega m$, $\rho_{Tl}=15 \times 10^{-8} \Omega m$), the ionic nature of the Te-Tl bond and fragmentation of the network on its addition. The variation in T_g in this glass system is also closely linked to the variation in the average bond energy of the system.

The tie line $Ge_{17}Te_{83-x}Tl_x$ is a Tellurium rich and the backbone of the glass is formed by $GeTe_{4/2}$ tetrahedral base units and Te-Te chains. It has been reported that thallium does not form bond directly with germanium but forms bonds only with tellurium atoms [9, 7, 10]. The addition of thallium atoms into the network, therefore leads to the replacement of existing Te-Te homopolar bonds by Te-Tl heteropolar bonds. In the $Ge_{17}Te_{83-x}Tl_x$ glass system, the possible bonds are Ge-Te, Ge-Ge, Te-Te, Te-Tl and Tl-Tl, which have the bond energies of 37.4 kcal/mole, 37.6 kcal/mole, 33.0 kcal/mole, 26.3 kcal/mole and 15.4 kcal/mole respectively [11, 12, 13]. Since the Te-Te bonds have more energy than the Te-Tl bonds, a simple bond strength approach may seem to favour the formation of Te-Te bonds but the chemically ordered network model states that the heteropolar Te-Tl bonds are formed first as they increase chemical order [14, 15].

NMR studies on glassy Tl-As-Se [16] as well as on crystalline thallium containing chalcogenides such as $TlGaSe_2$ [17, 18] indicate that Tl can exist as two species Tl^{1+} and Tl^{3+} . This approach can be considered in this present glass system also, assuming that Tl entered the network with two valences as Tl^{1+} and Tl^{3+} , the former being more ionic and the latter more covalent in nature. To vary the average bond energy with the same trend of the variation of switching voltage with Tl (figure 5), the numbers of Tl^{1+} and Tl^{3+} should be varied according to figure 6. The average

bond energy is the total bond energy of all the bonds divided by the total number of bonds. It is seen that for small x , thallium entered the network as Tl^{3+} but beyond a few numbers it was incorporated as Tl^{1+} .

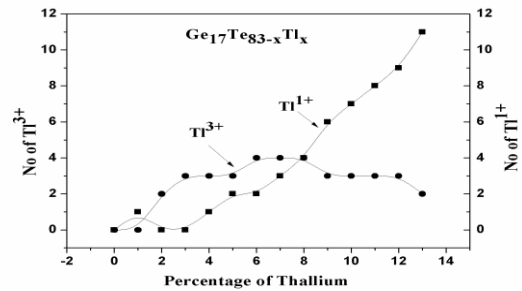


Figure-6: Variation in Tl^{3+} and Tl^{1+} numbers as a function of Thallium percentage. [8]

The Tl^{3+} initially replaces three Te-Te bonds and gives rise to a large reduction in the average bond energy. This is reflected in the steep fall in T_g and V_{th} in the initial part of the curves. By $x=6$, the number of Tl^{3+} has stabilised and the subsequently added thallium enters the network as Tl^{1+} which is more ionic and leads to the fragmentation of network. The change in average bond energy is much slower now as only one Te-Te bond is replaced by Te-Tl. The Ge-Te backbone is made up of $GeTe_{4/2}$ tetrahedra and Te-Te chains. The added thallium can bond with the Te on the tetrahedral to form $Tl^+Te^-GeTe^{3/2}$ units with a Tl^+Te^- dipole (as the electronegativity of Te is more than that of Tl) at one end or replace a bond in the Te chain region. The Tl^{1+} joined to such tetrahedra is terminal and the network is continued if another such unit aligns itself to form a quadrupole as shown in figure 7. For $x>6$, such quadrupoles occur higher in numbers and the net result of the reduction in average bond energy plus addition due to the attractive force between the quadrupoles is a very minimal change in T_g for larger atomic percentage of thallium.

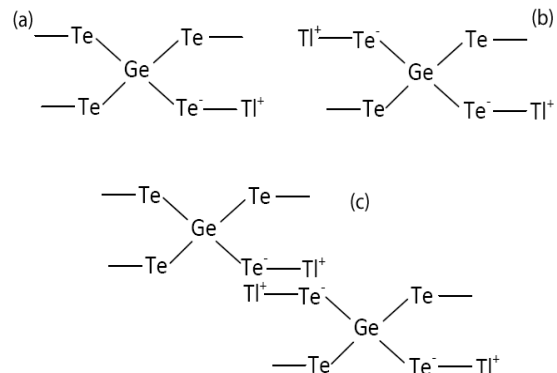


Figure-7 : Thallium containing units in the network glass- (a) Formation of a dipole. (b) Formation of two dipoles. (c) Formation of a quadrupole. [8]

Conclusion

The Addition of Thallium lowers the glass transition temperature T_g and the switching voltage V_{th} of $Ge_{17}Te_{83-x}Tl_x$ glasses much rapidly within the range of atomic percentage ($0 \leq x \leq 6$) of Tl. The factors contributing to this decrease is the ionicity of thallium and the fragmentation of the network. The average bond energy of the sample shows a decreasing trend and correlates well with the observed variation in V_{th} .

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