Electrical switching in germanium telluride glasses doped with Cu and Ag

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Abstract. Electrical switching in germanium telluride glasses containing metallic atoms (Cu and Ag) has been investigated. All these glasses are found to exhibit memory switching. The switching fields of these glasses are compared with the thermal parameters evaluated from DSC studies and the results are explained on the basis of the thermal model. The composition dependence of the switching field and the thermal parameters show interesting variations at the critical compositions which correspond to the rigidity percolation and the chemical thresholds of these glasses.

Chalcogenide glasses subjected to high electric fields often exhibit non-linear *I–V* characteristics. When the applied field attains a critical value, an unstable situation arises leading to a switching from a low-conducting state (OFF) to a high-conducting state (ON). This electrical switching is of two types, namely memory switching and threshold switching [1–3]. If the ON state observed in these materials is retained even after the applied field is reduced to zero, it is called a memory switching. Instead, if the material retraces its path to the original OFF state when the applied field is reduced to zero it is called a threshold switching. Threshold switching materials require a holding current and voltage to sustain the ON state. Once the holding current is removed, they revert back to their original OFF state. Thermally induced transitions (thermal mechanism) under high field explain the memory switching whereas the response of electrons to the applied high field (electronic mechanism) is used to explain the threshold switching [4–10].

The thermally induced transitions in a chalcogenide glass are amorphization, crystallization, and melting. The applied electric field accelerates the electrons and they emit phonons. This increases the temperature of the material due to Joule heating and the material crystallizes in between the electrodes [4, 8, 11]. Here the important point is how the resultant crystalline state occurs: by glass→crystal or glass→melt→crystal transformation. However, earlier microradiometer measurements give evidence for the later process [11–15]. Hence, the formation of a crystalline filament between the electrodes is important to observe memory switching in chalcogenide glasses. In turn, crystallization of these glasses depends on the properties of the material such as thermal diffusivity, network rigidity, chemical ordering, etc.

The metallic impurities such as copper and silver added to chalcogenide materials bring interesting variations in their properties. They enter the structural network of chalcogenide glasses in a special way and increase the network connectivity, crystallizing ability, and the electrical conductivity [16, 17].

In this work, *I–V* characteristics of Ge-Te glasses containing Cu and Ag have been studied. Differential scanning calorimetric (DSC) studies also conducted on these glasses to understand the thermally induced phase transitions. The general thermal model provides an understanding of the memory switching observed in these bulk glasses.

1 Experimental

$Cu_xGe_{15}Te_{85-x}$ $(0 \leq x \leq 10)$ and $Ag_xGe_{15}Te_{85-x}$ $(0 \leq x \leq 21.5)$ glasses are prepared by the conventional melt-quenching method. The amorphous nature of the samples prepared is confirmed by X-ray diffraction.

The samples polished to a thickness of 0.2 mm, are placed in between a point-contact top electrode and flat-plate bottom electrode, using a spring loading mechanism. To determine the *I–V* characteristics, a current is passed through the sample using a constant-current source. The voltage developed across the sample is measured by a digital voltmeter (DVM). The current through the sample is varied from 0–2 mA in a programmed manner and the *I–V* characteristics are obtained. The experimental arrangement is described in detail elsewhere [18]. DSC studies have been performed to evaluate the thermal parameters of these glasses.

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2 Results and discussions

2.1 Electrical switching and thermal mechanism

Figure 1 shows the *I–V* characteristics of $Cu_2Ge_{15}Te_{83}$ and $Cu_8Ge_{15}Te_{77}$ glasses. It can be seen that the current–voltage characteristics are linear initially (ohmic behaviour). At a critical voltage (V_{th}), a deviation from the ohmic behaviour and a negative-resistance region are observed which eventually leads to a high-conducting state. The samples are found to be latched on to this high-conducting state and do not revert back to their original high-resistance state. This observation clearly indicates that Cu-Ge-Te samples exhibit a current-controlled negative resistance with memory. These glasses are found to attain their original high-resistance state by applying a suitable current pulse.

I–V characteristics of $Ag_5Ge_{15}Te_{80}$ and $Ag_{21.5}Ge_{15}Te_{63.5}$ glasses are shown in Fig. 2, which indicates that these samples also exhibit a memory switching. Figure 3 shows the variation of switching field ($E_{th} = V_{th}/d$, where V_{th} is the threshold voltage for switching and '*d*' is the thickness of the sample) and crystallization activation energy (E_c) of $Cu_xGe_{15}Te_{85-x}$ as a function of composition [19]. Figure 4 shows the composition dependence of E_{th} and E_c of $Ag_xGe_{15}Te_{85-x}$ glasses [20]. Both Cu and Ag are very good conductors and their addition to Ge-Te glasses should reduce

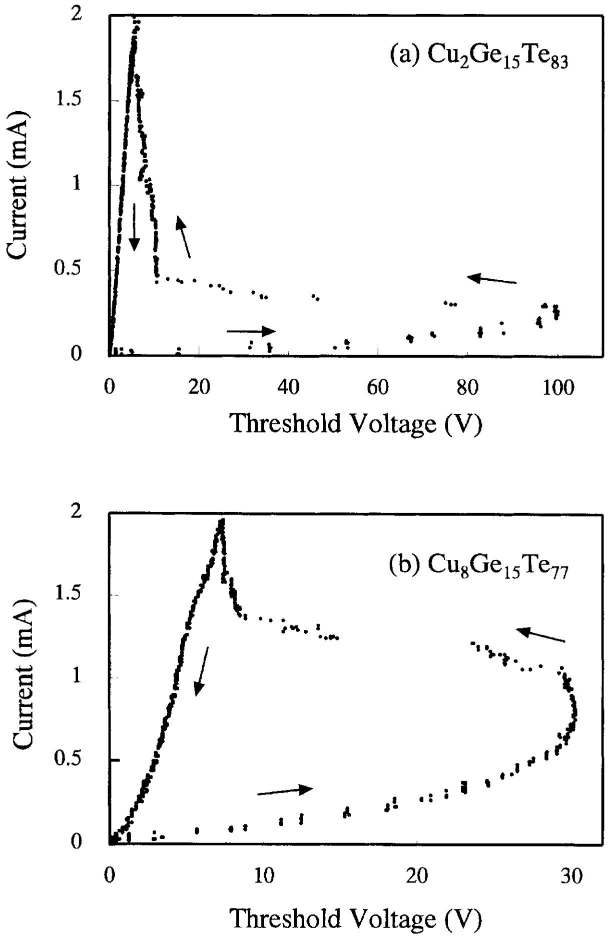

Fig. 1. $I - V$ characteristics $Cu_2Ge_{15}Te_{83}$ and $Cu_8Ge_{15}Te_{77}$ glasses

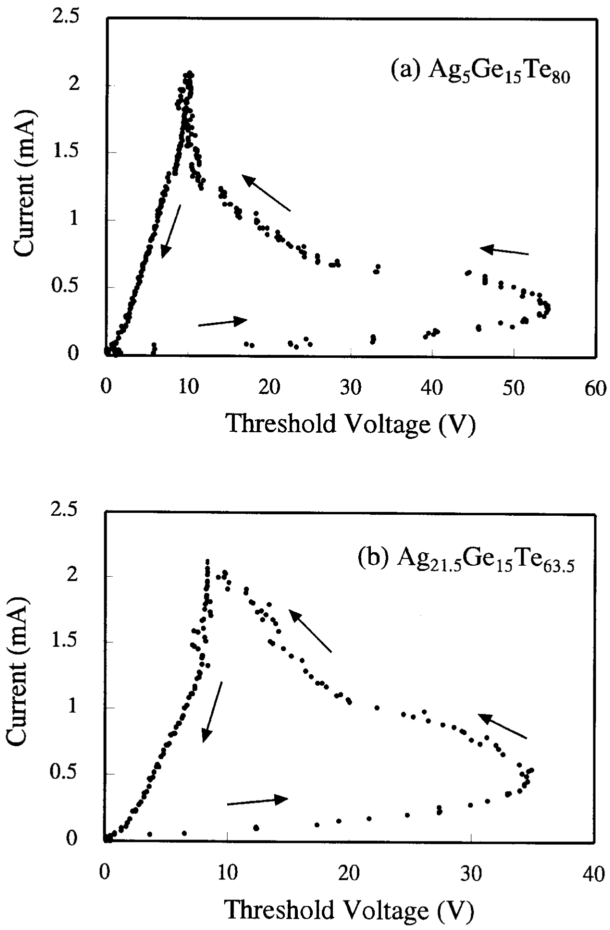

Fig. 2. $I - V$ characteristics of $Ag_5Ge_{15}Te_{80}$ and $Ag_{21.5}Ge_{15}Te_{63.5}$ glasses

E_{th}, which is seen in these figures. E_{th} of $Cu_xGe_{15}Te_{85-x}$ glasses decreases with an increase of Cu as in the case of the E_c, which can be seen from Figs. 3a and 3b. Both E_{th} and E_c exhibit an unusual jump-type variation at $x = 5$. In $Ag_xGe_{15}Te_{85-x}$ glasses, with an increase of Ag, E_{th} decreases and exhibits a slope change at $x = 5$. For $x > 12.5$, E_{th} continues to decrease with a smaller slope (Fig. 4a). The crystallization activation energy continues to decrease with x up to 5% of Ag, has a gradual increase for $5 \le x \le 18.5$, and has a jump decrease for $x > 18.5$.

The switching fields of Cu-Ge-Te and Ag-Ge-Te glasses are lower than the switching fields of As and Se doped Ge-Te glasses and comparable with the switching fields of As-Te glasses. For example, the switching fields of $Ge_{7.5}As_xTe_{92.5-x}$ glasses vary between 2–9 kV/cm [21]. $Ge_{21}Se_{17}Te_{62}$ glass switches at 9 kV/cm [22]. $Al_xAs_{40}Te_{60-x}$, and $As_{40}Se_xTe_{60-x}$ glasses have switching fields in the range 3–15 kV/cm [23, 24]. The switching fields of As_xTe_{100-x} glasses (2.3–5.5 kV/cm) are comparable with present Cu-Ge-Te and Ag-Ge-Te glasses [25]. In $As_{50}Te_{45}I_5$ glass the memory switching occurs at a field of 1.5 kV/cm [26]. The metal-doped As-Se glasses ($As_{30}Cu_xSe_{100-x}$) switch at very high fields of the order of 30 kV/cm [27]. It is also worth mentioning that $As_{30}Cu_xSe_{100-x}$ glasses for $x \le 15$ exhibit a memory switching whereas glasses with $x > 15$ exhibit an unusual behaviour of high-conducting ON state to a low-conducting OFF state [27, 28].

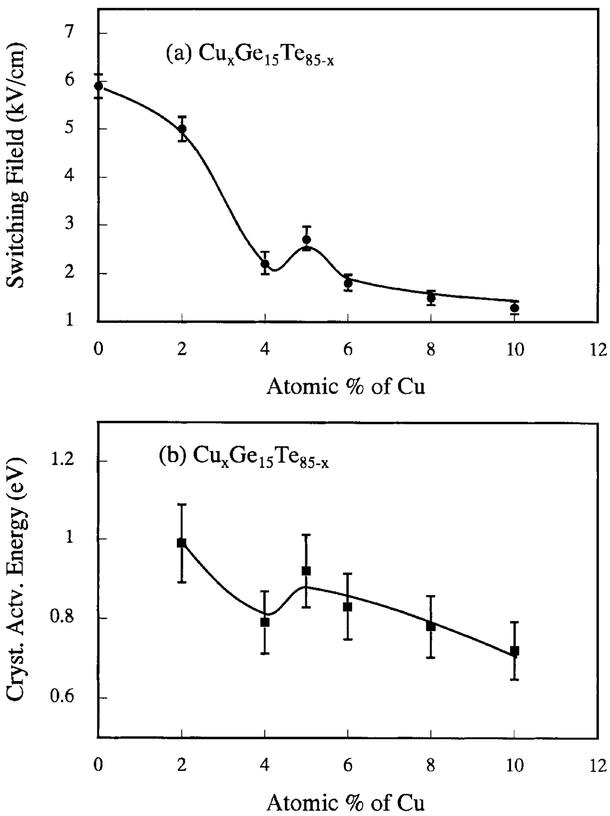

Fig. 3a,b. The composition dependence of switching field (**a**), and crystallization activation energy (**b**) of $Cu_xGe_{15}Te_{85-x}$ glasses

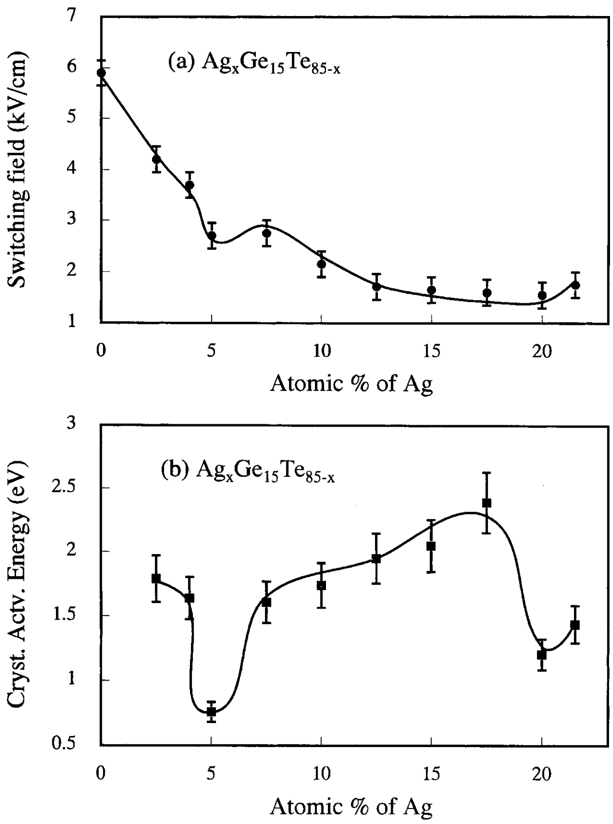

Fig. 4a,b. The composition dependence of switching field (**a**), and crystallization activation energy (**b**) of $Ag_xGe_{15}Te_{85-x}$ glasses

At the time of switching, the temperature of the sample increases considerably, and the material melts and cools to a conducting channel in between the electrodes. Interestingly, the resistivity of the glasses is found to decrease by many orders of magnitude when they undergo glass→crystal (heating) and liquid→crystal (cooling) transition [4]. Hence, crystallization is directly related to the switching mechanism.

Annealing of the $Cu_xGe_{15}Te_{85-x}$ samples at their crystalline temperatures results in GeTe and Te crystalline phases [19]. The samples crystallized from the melt (at 400 °C) also lead to the same crystalline phases. So the conducting crystalline filaments involved in the switching process probably consist of GeTe and Te phases. In $Cu_xGe_{15}Te_{85-x}$ glasses for $x < 5$, there are two melting reactions and they merge to a single melting at $x = 5$, at which E_{th} also shows a local maximum.

$Ag_xGe_{15}Te_{85-x}$ samples, when annealed at their crystallization temperatures, yield Ag_8GeTe_6, $GeTe_4$ and Te crystalline phases [20]. These glasses, upon heating, exhibit multiple-melting endotherms and they converge to a single melting for the highest content of silver. The observed switching field (E_{th}); crystallization temperature (T_c), and the melting temperature (T_m) of Cu-Ge-Te and Ag-Ge-Te glasses are given in Table 1.

In Ag-Ge-Te system, the crystalline phases that form around 330 °C (T_{m2}) and 380 °C (T_{m4}) correspond to a ternary eutectic $Ag_8GeTe_6 + GeTe + Te$ and a binary eutectic $Ag_8GeTe_6 + Te$, respectively [29]. It can be seen from the Table 1 that the ternary eutectic forms in the entire composition range, whereas the binary eutectic forms only in $x = 2.5$, 4, 5, and 10. The change in crystalline phases, around $x = 7.5$ and 10, reflects in E_{th} as a hump around $x = 7.5$ which can be seen from Fig. 4.

Table 1. Switching field (E_{th}) and thermal parameters of $Cu_xGe_{15}Te_{85-x}$ and $Ag_xGe_{15}Te_{85-x}$ glasses. E_{th} is given in V/cm and T_g, T_c, and T_m are given in °C

Cu	E_{th}	T_c	T_{m1}	T_{m2}	Ag	E_{th}	T_c	T_{m1}	T_{m2}	T_{m3}	T_{m4}
0	5900	247	–	415	2.5	4200	230	–	326	–	381
2	5000	225	367	387	4.0	3700	211	288	330	–	375
4	2200	216	367	392	5.0	2700	203	283	326	363	385
5	2700	230	370	–	7.5	2750	205	278	330	364	–
6	1800	225	365	–	10.0	2150	209	279	331	353	374
8	1500	213	370	–	12.5	1705	217	280	335	352	–
10	1300	188	371	–	15.0	1650	218	281	337	–	–
					17.5	1600	228	281	337	–	–
					20.0	1550	227	283	339	–	–
					21.5	1750	232	–	334	–	–

In the case of Cu-Ge-Te glasses, E_{th} seems to correlate with E_c (Figs. 3a and 3b). In this system, the crystalline phases formed at crystallization temperatures and from the melting temperatures are the same. Hence, in these glasses also the crystalline phases, which are formed from the melt, are responsible for the switching events.

Both $Cu_xGe_{15}Te_{85-x}$ and $Ag_xGe_{15}Te_{85-x}$ glasses show a small increase in switching fields around $x = 7.5$ at which the melting reaction around 380 °C also disappears. This melting reaction corresponds to a binary eutectic in Ag-Ge-Te glasses [29]. The binary eutectic occurs at 375 °C in Ge-Te system [4]. In Cu-Ge-Te also the reaction around 380 °C may correspond to a binary eutectic. The disappearance of this binary eutectic in both systems gives rise to the small increase in E_{th} at the respective compositions. This also indicates that the glass→melt→crystal transformation is responsible for the switching process in Cu-Ge-Te and Ag-Ge-Te glasses.

Generally, the switching field for memory and threshold switching decreases under external influences of high pressures and high temperatures. At high temperatures the conductivity of the glasses increases. The structural modification and crystallization of these glasses becomes easy under high pressure and high temperature, which can help them to switch, when subjected to high fields. For example, Ge-As-Se, an excellent glass former with a wide range of glass formation, does not exhibit switching at normal conditions. At high temperatures (275 °C) $Ge_{30}As_{20}Se_{50}$ glass exhibits a threshold switching [12]. The threshold voltage for memory switching in $As_{50}Te_{45}I_5$ decreases from 20 V at atmospheric pressure to 3 V at a pressure of 16 kbar [26].

The time-temperature-transformation (TTT) diagrams are generally used to explain the thermally induced phase transitions in amorphous systems [30, 31]. For example a schematic TTT diagram showing the quench rates that will produce glass sample (dot line) and a crystallized sample (dash line) is shown in Fig. 5.

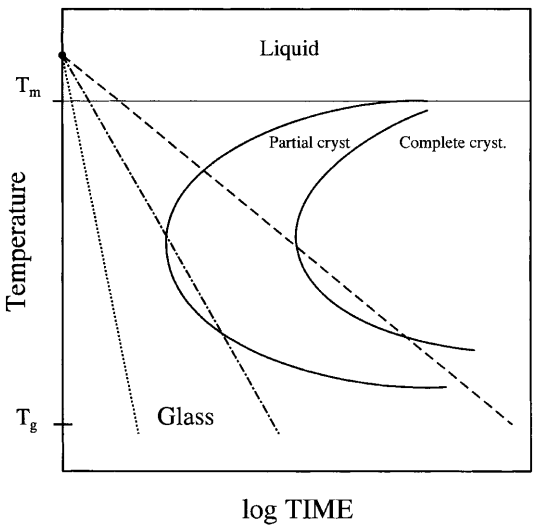

Fig. 5. Schematic TTT curves showing quench rates that will produce a glassy sample (*dot line*), a partially crystallized sample (*dot-dash line*), and a completely crystallized sample (*dash line*)

When the temperature of the melt is decreased the time scale for crystallization decreases. In the super-cooled liquid the time scale for the internal relaxation increases when the temperature is decreased and reaches the order of 10^2 s, when the temperature enters the glass-transformation range by avoiding the crystallization. If the internal relaxation time is smaller than the crystallization time, the system will rapidly move towards the crystalline state. There is a temperature at which the crystallization is maximum. This temperature fixes the knee of the TTT curve. To obtain a glassy state the rate of quenching should be fast (dotted line) in such a way that it clears the knee of the TTT curve. If the quench rate is slow (dash line) one has a crystalline state. If the quench rate lies just above the knee of the TTT curve (dot-dash line) the system attains a partial crystalline state and one has a memory-switching possibility. At the critical field (switching field), filaments of the bulk Cu-Ge-Te and Ag-Ge-Te glasses get heated, undergo glass→melt transformation, and then cool fast. The quench rates of the filament appear to lie just above the knee of the TTT curve. This partial crystallization probably results in the memory switching in Cu-Ge-Te and Ag-Ge-Te glasses.

2.2 *Critical compositions in* Cu-Ge-Te *and* Ag-Ge-Te *glasses*

It has been suggested that the chalcogenide glasses consist of under-cross-linked floppy and over-constrained rigid networks. A transformation from floppy to a rigid network occurs at a critical composition corresponding to the average coordination number $Z_{av} = 2.40$, called rigidity percolation threshold [32]. In addition to the rigidity percolation threshold, a chemical ordering also occurs in chalcogenide glasses, where the structural network is maximally ordered [21]. Unusual changes in various properties are expected at these critical compositions. Switching fields as a function of composition in Ge-As-Te and Al-Te glasses exhibit anomalies at the critical compositions [21, 33].

It is interesting to note that both $Cu_xGe_{15}Te_{85-x}$ and $Ag_xGe_{15}Te_{85-x}$ glasses exhibit the rigidity percolation which can be seen from the unusual change (Figs. 3 and 4) in their switching field at $x = 5$ ($Z_{av} = 2.40$). In addition, Ag-Ge-Te glasses exhibit a minimum at $x = 20$ ($Z_{av} = 2.70$), which corresponds to the chemical threshold (Fig. 4). The chemically ordered network has the maximum molar volume and minimum density [32]. The maximum ordering in the network indicates that they are closest to its crystalline state. Hence, crystallization of the chemically ordered network requires minimum energy resulting in a lesser switching voltage. The thermal properties of Cu-Ge-Te and Ag-Ge-Te glasses also show unusual changes at these critical compositions [19, 20].

3 Conclusions

The current–voltage characteristics of $Cu_xGe_{15}Te_{85-x}$ and $Ag_xGe_{15}Te_{85-x}$ glasses are found to exhibit memory switching. The switching fields of these glasses are found to decrease with the increase of Cu and Ag. The thermal model explains the memory switching observed in these glasses.

The TTT diagram explaining the thermally induced phase transitions in amorphous systems is used to explain the memory switching observed in the present glasses.

The switching fields of Cu-Ge-Te and Ag-Ge-Te glasses exhibit anomalies at the critical compositions corresponding to the rigidity percolation and chemical ordering thresholds.

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