

Anomalous electrical switching behaviour in phase-separated bulk Ge-Se-Ag chalcogenide glasses

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Abstract. – Bulk, Se-rich $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ ($0 \leq x \leq 0.20$) glasses show anomalous electrical switching behaviour which is attributed to difference in the thermal conductivities of Ag_2Se inclusions and GeSe base glass. The present results also show that there is a sharp drop in switching voltage with silver addition, which is due to the higher metallicity of silver and the presence of Ag^+ ions. Further, the leveling of threshold voltage (V_T) around $x = 0.10$, is associated with the percolation of Ag_2Se phase in the Ge-Se matrix.

Phase change memories based on chalcogenide glasses have found resurgence in interest in the recent times. These data storage devices make use of reversible and irreversible switching exhibited by glassy chalcogenides induced by an electric field, light or both [1–3].

The phenomenon of electrical switching in chalcogenide glasses was first observed by Ovshinsky nearly three decades ago [4]. Chalcogenide switches are normally classified into two groups, namely threshold (mono-stable) or memory (bi-stable) devices depending on the type of switching (reversible or irreversible, respectively) exhibited by them. Electrical switching in these materials occurs when an appropriate voltage, known as the threshold voltage (V_T), is applied and the glass switches to a high conducting ON state from a low conducting OFF state. On the removal of the switching field, threshold switching glasses revert to the OFF state whereas memory switches remain locked to the ON state.

The process of switching in both threshold and memory glasses is primarily electronic in nature and it occurs when the charged defect states in a chalcogenide glass are filled by the field-injected charge carriers. However, additional thermal effects come into play in memory materials which result in the formation of a conducting crystalline channel [5]. Phase change memories make use of chalcogenide glasses of memory switching type. It has also been recently pointed out that certain glasses can be repeatedly switched electro-optically, by applying $0.4\text{--}0.6 V_T$ and irradiating with appropriate light [6].

Studies on the switching behavior of chalcogenide glasses help us in identifying suitable glasses for different applications including phase change memories, data storage devices etc.

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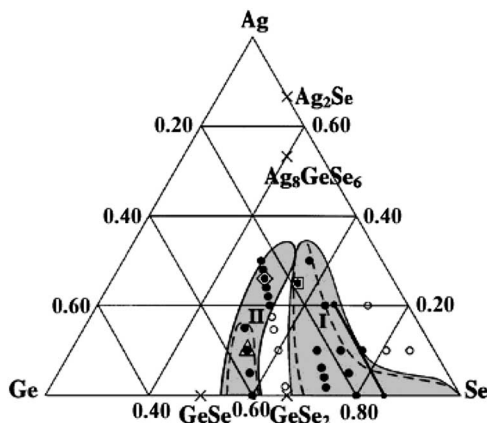


Fig. 1 – The phase diagram of the Ge-Se-Ag ternary system showing the glass-forming regions [7].

The present work deals with the studies on electrical switching characteristics in Se-rich $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ ($0 \leq x \leq 0.20$) glasses. These glasses are found to be microscopically phase separated, containing Ag_2Se clusters embedded in a GeSe backbone [7–9]. With increasing silver concentration, the Ag_2Se phase percolates in the Ge-Se matrix, with a well-defined percolation threshold at $x = 0.10$. This silver phase percolation in the GeSe base glass is likely to be responsible for the sharp transition from semiconductive to ionic character of Se-rich Ge-Se-Ag glasses [10, 11].

Figure 1 shows the glass-forming regions in the Ge-Se-Ag ternary system [8]; the Se-rich and Ge-rich glasses are denoted by I and II, respectively. The solid black line in the Se-rich region I shows the composition tie-line chosen for the present work. Bulk $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses ($0 \leq x \leq 0.20$) have been prepared by vacuum-sealed melt-quenching method. Appropriate quantities of high-purity (99.99%) constituent elements are sealed in an evacuated quartz ampoule (at 10^{-5} Torr) and slowly heated in a horizontal rotary furnace. The ampoules are maintained at 1000°C and rotated continuously for about 24 hours 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 of the quenched samples is confirmed by X-ray diffraction.

The switching behavior of sample is studied by recording I - V characteristics using Keithley Source Meter (Model 2410) 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 and a point-contact electrode made of brass. A constant current is passed through the sample to record voltage developed across sample.

It has been found in the present study that $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses of lower silver concentration ($x = 0.07$ and 0.08) do not exhibit switching at voltages up to 1100 V. At voltages below 1100 V, negative-resistance behavior and switching is seen only in $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ samples with $x \geq 0.09$. Figure 2 shows the I - V characteristics and switching behavior of $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses ($x \geq 0.09$), which indicates that these glasses exhibit an initial Ohmic behavior in the I - V characteristic. At a threshold voltage V_T (corresponding to a threshold current I_T), the samples switch from a high-resistance OFF to a low-resistance ON state. Compared to other chalcogenide glasses, the switching in $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses has been found to be not ideal with fluctuations seen in the I - V characteristics (fig. 2).

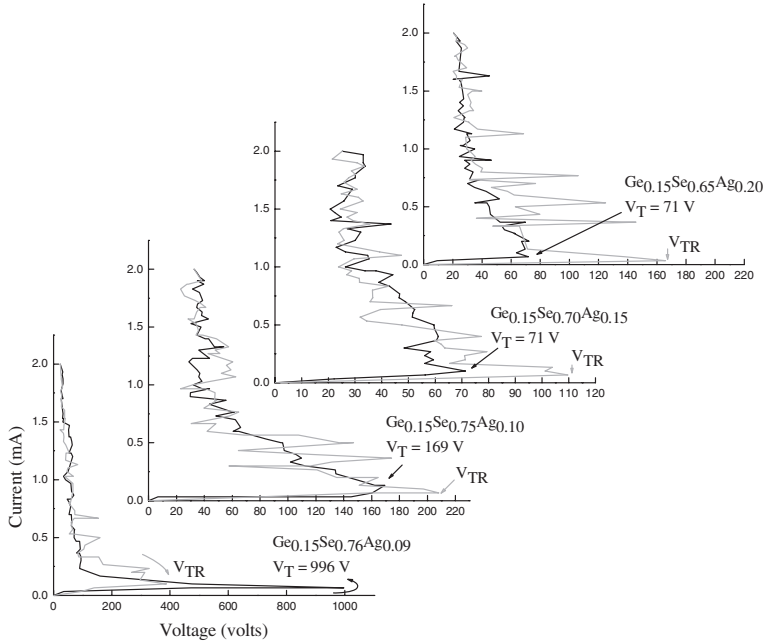


Fig. 2 – The current-voltage characteristics of $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ ($0.09 \leq x \leq 0.20$) glasses of different compositions.

Upon reducing the current in the ON state, Ge-Se-Ag samples studied have been found to revert back to the high-resistance state which indicates that these samples exhibit threshold switching behavior. The samples can be repeatedly switched between the high-resistance OFF and the low-resistance ON states with switching voltages reproducible within $\pm 5\%$.

The holding voltage V_{TR} (corresponding to the holding current I_{TR}) at which samples revert back to the high-resistance state is usually less than or equal to the threshold voltage V_{T} . However, in the $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ system, it is found that $V_{\text{TR}} > V_{\text{T}}$ for glasses with higher Ag content and the difference increases with Ag concentration. The fluctuations in the I - V characteristics are also more for samples with higher silver proportions.

The variation of the threshold voltage (V_{T}) of $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses with silver concentration is shown in fig. 3. It can be seen from this figure that the switching voltage of $\text{Ge}_{0.15}\text{Se}_{0.77}\text{Ag}_{0.08}$ sample is around 1000 V. With further addition of silver, the switching voltages abruptly drop to about 200 V for $\text{Ge}_{0.15}\text{Se}_{0.75}\text{Ag}_{0.10}$ glass; V_{T} becomes almost independent of silver addition, beyond $x = 0.10$.

The earlier studies on Ge-Se-Ag glasses reveal that there are two distinct glass-forming regions in this system [8, 9, 12, 13]; the Se-rich glasses are found to be ionic whereas Ge-rich glasses are semiconductive. Further, the Se-rich $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses are microscopically phase-separated and composed of Ag_2Se clusters and a Ge-Se network, which can be described by [8, 9]

$$\text{Ge}_y\text{Se}_{(1-y)-x}\text{Ag}_x = \left(\frac{x}{2}\right) \text{Ag}_2\text{Se} + \left(1 - \frac{x}{2}\right) \text{Ge}_t\text{Se}_{1-t},$$

where

$$t = \frac{y}{\frac{x}{2} + y}.$$

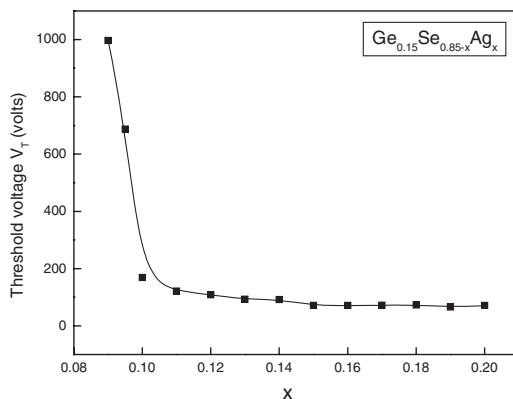


Fig. 3 – The variation of switching voltages (V_T) with Ag content for $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ ($0.09 \leq x \leq 0.20$) glasses.

With increase in silver concentration, the Ag_2Se phase is found to percolate in the Ge-Se matrix with the concentration $x = 0.10$ corresponding to the silver phase percolation threshold. The signature of this silver phase percolation is observed in various experiments like alternating differential scanning calorimetric (ADSC) [9] and modulated differential scanning calorimetric (MDSC) studies [8], Raman Scattering measurements [8], etc. The sharp fall in V_T and its saturation around $x = 0.10$, can be connected with the percolation of the Ag_2Se phase in the parent glass.

The initiation of switching in chalcogenide glass is generally understood by an electronic model [14]; According to this model, switching occurs when field-injected charge carriers completely fill up the charged defect states existing in these materials (C_3^+ and C_1^-), known as the valence alternation pairs (VAPs) [15]. Here, C represents the chalcogen and the subscript and superscript denote the coordination and the charge state, respectively. In memory samples, a consequential crystalline channel forms due to the Joule heat generated by the collision between the surging free electrons and the lattice.

In $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses, in addition to VAPs, mobile Ag^+ cations are also present in the super-ionic Ag_2Se phase. The presence of the Ag_2Se phase and the Ag^+ cations influence the switching characteristics of these glasses in two ways. 1) The Ag_2Se inclusions in the GeSe base glass can cause current crowding. As the Ag_2Se phase is more conductive than the GeSe base, it draws most of the current. As a result, heat is generated essentially around the periphery of the Ag_2Se clusters, leading to local melting in that region. The process of local melting and the subsequent re-solidification mainly depends upon the thermal conductivities of the Ag_2Se inclusions and the GeSe base glass. We believe that the local melting (and the subsequent re-solidification) is responsible for the fluctuation present in the current-voltage characteristics of the $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ glasses (fig. 2).

2) The migration of Ag^+ ions also plays a crucial role in the switching behavior of Ge-Se-Ag glasses. In the OFF state, the following recombination processes dominate: a) the hole capture by C_1^- centers ($\text{C}_1^- + e^+ \rightarrow \text{C}_1^0$) and b) the electron capture by C_3^+ centers ($\text{C}_3^+ + e^- \rightarrow \text{C}_3^0$). The Ag^+ ions present in the sample can be involved in the passivation of C^- centers (process a)) through diffusion [8], thereby reducing the voltage required to initiate the switching effect and also the time taken to switch the sample. The sharp decrease in the V_T with the addition of silver can be understood based on both the higher metallicity of silver and faster passivation of charged defect states.

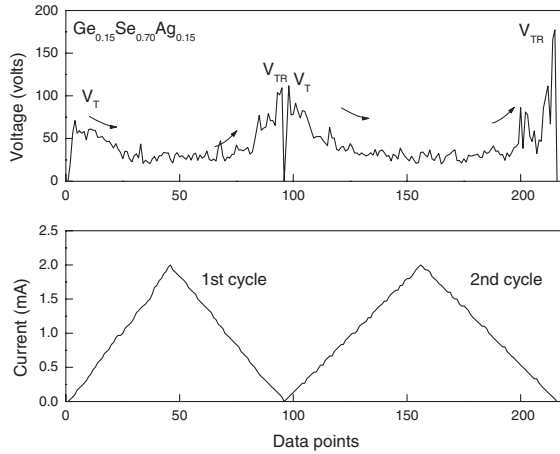


Fig. 4 – The voltage response of $\text{Ge}_{0.15}\text{Se}_{0.70}\text{Ag}_{0.15}$ sample with applied current (positive cycle).

In the ON state, Ag^+ ions move towards the negative electrode under the influence of the applied electric field. Due to the heavier mass of silver atoms and their lower mobility, a space-charge build-up takes place near the cathode. The higher holding voltage required to revert back to the OFF state ($V_{TR} > V_T$) upon reducing the current in the ON state, is the consequence of the space charge build-up. Further, the larger V_{TR} seen in samples having larger silver proportions is consistent with the earlier results which indicate that $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ samples with larger silver concentrations ($x \geq 0.10$) are primarily ion-conducting [8, 9]. In our view, this type of behavior is likely to be seen in all samples where ionic conductivity is dominant compared to electronic conductivity.

It is interesting to note that a similar type of movement of Ag^+ ions has been reported in chalcogenide electrolyte films; the ion current occurs in the electrolyte if an oxidizable electrode

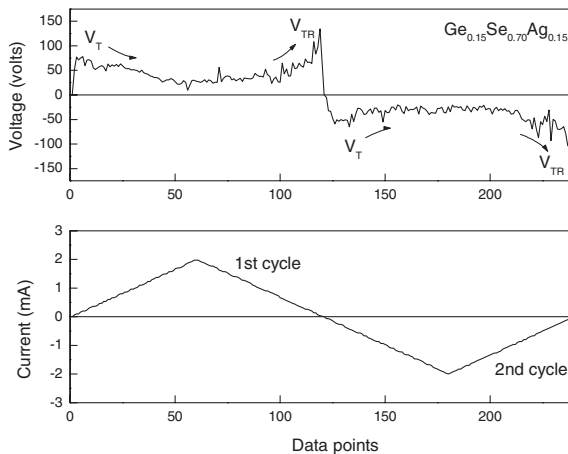


Fig. 5 – The voltage response of $\text{Ge}_{0.15}\text{Se}_{0.70}\text{Ag}_{0.15}$ sample with applied current (positive and negative cycle).

(anode) is made positive with respect to an opposing electrode (cathode) and sufficient bias, typically greater than a few hundred millivolts, is applied [16].

To confirm the role played by the Ag^+ ions, repeated switching cycles have been performed on the same sample. After the first switching cycle, the accumulation of Ag^+ ions near the negative electrode will increase and, as a result, the threshold voltages are to increase in the subsequent cycles (fig. 4).

We have also conducted positive and negative cycles successively on the same sample (fig. 5). It can be observed from fig. 5 that during 2nd negative cycle, switching characteristics follow the 1st positive cycle. As Ag^+ ions move towards opposite electrodes during the next cycle, switching characteristics follow the previous cycle.

In conclusion, Se-rich $\text{Ge}_{0.15}\text{Se}_{0.85-x}\text{Ag}_x$ ($0 \leq x \leq 0.20$) glasses are found to exhibit an anomalous electrical switching behaviour. Fluctuations are observed in the I - V characteristics of these samples, which has been attributed to the difference in thermal conductivities between the Ag_2Se inclusions and the GeSe base glass. A sharp drop has been observed in the switching voltage with Ag concentration which is due to the more metallic nature of silver and the presence of Ag^+ ions. Further, the saturation in the decrease of V_T around $x = 0.10$, is related to silver phase percolation in these glasses, which has been proposed earlier on the basis of experiments such as Alternating Differential Scanning Calorimetry (ADSC), Raman Scattering, etc.

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