Signature of a silver phase percolation threshold in microscopically phase separated ternary Ge$_{0.15}$Se$_{0.85}$–xAg$_x$ (0 ≤ x ≤ 0.20) glasses

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The interest in superionic glasses has increased considerably in the recent years because of the potential application of these materials in different fields. Glasses on the selenium-rich side of the Ge–Se–Ag system are fast ionic conductors with silver as the mobile cation. Although several studies have been undertaken on Ag-doped chalcogenide glasses, especially on Ge–Se–Ag systems, the microscopic structure of these glasses is not fully understood.

Figure 2(a) displays the reversible heat flow curves in the ADSC scan of Ge$_{0.15}$Se$_{0.85}$–xAg$_x$ glasses. In all the curves, two endothermic glass transition peaks can be seen which show the heterogeneity of these glasses. Among these two, the lower glass transition peak T$_g^1$ systematically shifts up with the increase in Ag concentration. The higher glass transition peak T$_g^h$ does not shift much, but increases in strength with the increase in Ag concentration. It is seen in the present study that ΔC$_p$ values of Ge–Se–Ag glasses, estimated from T$_g^h$, generally increases with Ag content and the increase becomes sharper at Ag=0.10 [Fig. 2(b)]. When the concentration of Ag is increased beyond 0.15, it is very difficult to distinguish the two glass transitions. If these samples are rerun in the ADSC, as suggested earlier, only the first glass transition T$_g^1$ is observed as the second phase has already crystallized.

Figure 3(b) shows the nonreversible heat flow curves of Ge$_{0.15}$Se$_{0.85}$–xAg$_x$ glasses in ADSC scans. One can discern two exothermic crystallization peaks (T$_c^1$ and T$_c^2$), at higher
Ag concentrations (x ≥ 0.10), an important observation, which will be discussed later. It is also seen that the strength of both exothermic peaks increases systematically with Ag concentration afterwards.

Powder x-ray diffraction studies (using the Cu K\textsubscript{α} line with λ = 1.5405 Å) of bulk glasses are taken after annealing at 320 and 450 °C (after the completion of crystallization reactions at T\textsubscript{c1} and T\textsubscript{c2}, respectively) for several minutes to several hours to find out the products of the crystallization reactions. The x-ray reflections can be indexed for cubic Ag\textsubscript{2}Se and c-Ag\textsubscript{8}GeSe\textsubscript{6} phases in samples annealed at 320 °C, but only c-Ag\textsubscript{8}GeSe\textsubscript{6} is found in samples annealed at 450 °C (Fig. 4).

Density, molar volume, and microhardness studies are also carried out to find out the impact of the change in the microscopic structure of Ge–Se–Ag glasses. The density of the glasses is measured using a density measurement kit (model AG64, METTLER TOLEDO) with distilled water and CH\textsubscript{3}OH as reference liquids. The error in the density is estimated to be less than 2%. The Vickers microhardness of the samples is measured with an accuracy of ±5%, with a hardness tester (model HMV-2000, SHIMADZU). A pyramidal diamond indenter is used with an applied load of 50 g for 10 s. It is seen from the above measurements that a sharp transition is exhibited in the composition dependence of density, molar volume, and microhardness, around x = 0.10 [Figs. 5(a) and 5(b)].

Bimodal glass transitions of Se-rich Ge–Se–Ag glasses are attributed to Ge–Se backbone and Ag\textsubscript{2}Se inclusions.\textsuperscript{5,6} As mentioned earlier, in the rerun of the samples, only one T\textsubscript{g} which corresponds to Ge\textsubscript{0.15}Se\textsubscript{0.85} backbone is seen. However, it has been found that the glass transition temperatures in the second runs are marginally higher than those of the first runs [Fig. 3(a)]. Further, in the second runs, no crystallization reaction is observed (Fig. 6). This confirms that the two crystallization reactions observed are not related to Ge\textsubscript{0.15}Se\textsubscript{0.8} backbones, contrary to the results obtained in Ref. 4, where T\textsubscript{c1} and T\textsubscript{c2} are attributed to c-Ag\textsubscript{8}GeSe\textsubscript{6} and c-GeSe\textsubscript{2}, respectively.

As mentioned above, T\textsubscript{c1} and T\textsubscript{c2} correspond to the crystallization of the Ag\textsubscript{2}Se and Ag\textsubscript{8}GeSe\textsubscript{6} phases, respectively (Fig. 4). As T\textsubscript{c1} and T\textsubscript{c2} are close by, annealing at T\textsubscript{c1} shows mainly c-Ag\textsubscript{8}GeSe\textsubscript{6} peaks along with cubic Ag\textsubscript{2}Se peaks which is formed as per the following reaction, suggested earlier:\textsuperscript{5}

\[
4(\text{Ag}_2\text{Se}) + \text{GeSe}_2 = \text{Ag}_8\text{GeSe}_6.
\] (1)

A simple crystallization scheme for the formation of the Ag\textsubscript{8}GeSe\textsubscript{6} phase is as follows:
Ge$_y$Se$_{1-y}$Ag$_x$ = S$_x$D$_8$Ag$_8$GeSe$_6$ + S$_{1-x}$D$_8$Ge$_{8-t}$Se$_{1-t}$, 

where

$t = \frac{y}{1-x} \left( \frac{6x}{8} + 1 \right) - x \frac{1}{1-x}$.

In Eq. (2), the first term on the right-hand side designates the Ag$_2$Se additive glass phase and the second term to the remaining base-glass phase.

Figure 7(a) shows that $T_g^1$ increases systematically with Ag concentration as the Ge$_{0.15}$Se$_{0.85}$ base glass becomes progressively Se deficient (and Ge-rich) as per Eq. (2), which is in agreement with the earlier result that the glass transition temperature of Ge$_x$Se$_{1-x}$ glasses increases with Ge content, for compositions $y \leq 0.33$ (Ref. 10 and 11). Further, Mössbauer studies suggest that Ge$_y$Se$_{1-y}$ glasses are mainly comprised of Ge(Se$_{1/2}$)$_4$ tetrahedral units for compositions $y < 0.33$ (Ref. 12). Recent NMR studies on Ge$_y$Se$_{1-y}$ glasses also reveal the presence of Ge(Se$_{1/2}$)$_4$ tetrahedra and Se chains up to $y = 0.33$, without any Ge–Se–Se bonding. As a result, inclusion of Ag in Se-rich Ge$_y$Se$_{1-y}$ glasses creates mainly Ag$_2$Se phases. Based on the above, the phase-separated Ge–Se–Ag glasses can be described by

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

where

$t' = \frac{y}{x + y}$.

While heating up to 450 °C, the Ag$_2$Se phase crystallizes as Ag$_8$GeSe$_6$ following Eq. (1).
signature of the percolation threshold for the Ag$_2$Se phase in these phase-separated glasses. At this concentration, the Ag$_2$Se clusters embedded in Ge$_{0.15}$Se$_{0.85}$ base become homogeneous throughout the glass.

Studies on the variation of density, molar volume and microhardness of Ge$_{0.15}$Se$_{0.85-x}$Ag$_x$ glasses also show sharp transition at the Ag-phase percolation threshold [Figs. 5(a) and 5(b)]. As the Ag$_2$Se inclusions in Ge$_{15}$Se$_{85}$ backbone become homogeneous, the density of total network increases sharply above $x=0.10$. For the same reason, a sudden reduction in the molar volume is found at this concentration. The appearance of $T_{c1}$ and $T_{c2}$ beyond Ag concentration of 0.10, clearly indicates the increase in the fragility of these glasses. Microhardness measurements are also in good agreement with this concept [Fig. 5(b)].

Percolation threshold of Ag$_2$Se phase embedded in Ge$_{15}$Se$_{85}$ base is likely to be responsible for the sharp transition from semiconductive to ionic character of Se-rich Ge–Se–Ag glasses.$^{14,15}$ This reestablishes the fact that structural heterogeneity or granularity is the main criterion for ionicity in glasses.

Impact of silver phase percolation in electrical properties of these glasses is also exemplified in a sharp transition in the switching voltages at Ag=0.10, which will be discussed in more detail in forthcoming publications.$^{16}$

In summary, the present study shows that Ge$_{15}$Se$_{85-x}$Ag$_x$ glasses are microscopically phase separated and composed of Ag$_2$Se clusters and GeSe$_2$–Se network. When Ag concentration exceeds 10%, the Ag$_2$Se clusters embedded in the GeSe$_2$–Se network percolates. The signature of this percolation threshold is clearly observed as the sudden appearance of two exothermic crystallization peaks in ADSC runs. Density, molar volume, and microhardness studies also strongly support this view of a percolation transition. The superionic conduction observed earlier in these glasses at higher silver proportions is likely to be connected with the silver phase percolation.

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