

CHAPTER 20

Synthesis and Thermal Properties of Indium Additive Based Some Multi-Component Chalcogenide Glasses

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Abstract: $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($0 \leq x \leq 15$) multi-component glassy alloys have been studied using differential scanning calorimetric (DSC). Thermal properties of these chalcogenide glasses (CGs) analysed by differential scanning calorimetry. Using T_g , T_c , and T_p values at a heating rate of 10K/min, the weighted glass thermal stability, H_w , stability parameter, S , and fragility index have been computed. I have also discussed the composition dependence of the fragility index, thermal stability parameter, S , and weighted glass thermal stability, H_w . This can be explained by using Phillips and Thorpe's constraint theory for chalcogenide glasses.

Keywords: Multi-component chalcogenide glasses, Differential scanning calorimetric (DSC), thermal stability (weighted glass,) H_w , and stability parameter S , fragility index.

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1. Introduction

Chalcogenide glasses represent a category of amorphous semiconductors that include one or more chalcogen elements, specifically selenium (Se), tellurium (Te) and sulphur (S), which are originate in group VI of the periodic table. These elements essentially have covalently molecular arrangements, and they have a strong propensity for their bonds to join collectively to form rings and chains. The composition of these glasses involves the incorporation of various elements, such as Ge, As, Sb, Sn, In, Cd, and others. These materials exhibit low phonon energy and typically demonstrate transparency across the visible spectrum extending into the infrared range. When compared to traditional oxide glasses, chalcogenide glasses usually show noticeably less mechanical strength and thermal stability. They do, however, exhibit higher order optical non-linearity, a broad range of infrared transparency, a higher refractive index, and more thermal expansion. Selenium-based semiconducting glasses are of particular importance since they are especially used in digital X-ray imaging and currently as photoconductors in high-definition TV pickup tubes. Recently, interest in semiconductor alloys based on Se–Te from both a scientific and technological standpoint. Even when they are believed to be appropriate compositions for phase-change memory materials, they cause serious problems when used in optical phase-change devices as a recording layer.^{1,2}

The exceptional thermal, optical and electrical, properties of (CGs) which may be altered by altering their chemical composition have drawn a lot of interest in recent decades. Chalcogenide glasses are based on covalently bound two, three, and four-coordinated building blocks. The electrical, thermal, and optical properties of these glasses are significantly influenced by the alloying concentration. These glasses have been found to exhibit a chemical threshold at a particular alloy percentage. Few investigations have been conducted on multicomponent chalcogenide glasses; the majority of previous research on chalcogenide glasses has concentrated on binary and ternary systems.³⁻¹⁰ Recent research on these glasses has mostly concentrated on greater metallic chalcogen alloys in an effort to create more stable and durable chalcogenide glasses.

Researchers have been synthesising alloying elements, especially VI-III (like Se and In) and VI-III-IV-II (like Se, Te, In, and Cd) groups, more quickly in recent years due to increased scientific and technological interest in the field of chalcogenides.¹¹⁻¹⁵

New multi-component (CGs) has attracted a lot of attention lately, both from the perspective of fundamental physics and for use in innovative device technologies. Se-rich binary and ternary chalcogenide glassy alloys are known for their, enhanced hardness, decreased aging effect, high resistivity, optical and enhanced electrical properties, and good routine. Nevertheless, there are certain disadvantages to ternary glasses that imply their restricted application. GeBiSeTe, Al(Ge-Se-Y), GeAsSeTe, Cd (Zn)Ge(As), GeSe₂Sb₂Se₃PbSe, Cu₂ZnSnSe₄, and other metal and semimetal-containing glassy alloys are particularly appealing study materials.¹⁶⁻¹⁹ In this glassy Se-Te-Cd-In system's I have reported thermal stability, Hw, thermal stability (weighted glass) stability parameter, S, and fragility index.

2. Experiment techniques

The elements were measured according to their atomic percentage of weight proportions and were found to be of high purity (99.999%) using an electronic balance. The materials were expelled using 8 cm long with 12 mm inner diameter quartz ampoules. The sample ampoules were sealed at a vacuum of 10^{-5} torr for 10-12 hours, and then heated to 825 °C at a rate of 3–4 K/min in an electronic furnace to exclude the possibility of glassy alloys interacting with oxygen at a high temperature. The samples were shaken frequently to ensure their homogeneity. The alloys in their glassy state were then created by quickly quenching the molten samples in ice-cooled water.

In order to confirm as-prepared alloys are glassy, the X-ray diffraction pattern of the samples was obtained using a model Philips PW 1700 powder diffractometer that operated at 20 keV with Cu-K α ($\lambda = 1.54056$ Å) radiation. Figure 1 shows the Se₇₅Te₁₀Cd₁₀In₅ glass's XRD pattern. A DSC device (Shimadzu DSC-60) was used to examine each sample's thermal behaviour. Usually, 10 mg of the powdered material was heated at four different rates, in conventional aluminium pans. The heat that was occupied in or formed during phase transitions was measured using differential scanning calorimetry (DSC), which was also utilised to investigate the kinetics of glass transition and crystallisation in non-isothermal conditions. Thermal analyzer's microprocessor has, the temperature precision was ± 0.1 K, and the heat flow accuracy was ± 0.01 mW.

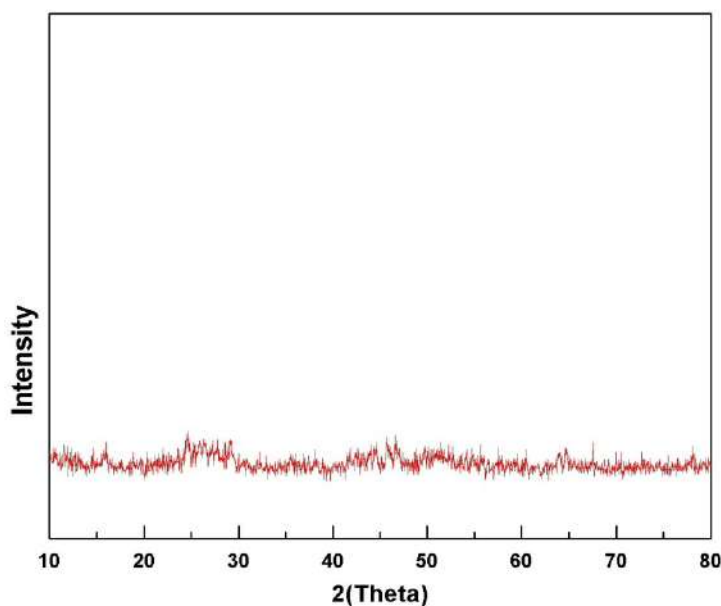


Fig. 1. XRD pattern of Se₇₅Te₁₀Cd₁₀In₅ chalcogenide glass

3. Results

The study of the glass transition and crystallization kinetics has made significant use of the non-isothermal DSC technique in the literature [20–24]. Because of its (i) simplicity of use, (ii) modest sample preparation, (iii) extremely sensitive, and (iv) relative independence from sample geometry, this technique is particularly important. Consequently, we have used the DSC technique to examine thermal stability in our current work. Typical DSC thermograms of $\text{Se}_{75}\text{Te}_5\text{Cd}_{10}\text{In}_{10}$ chalcogenide glass obtained at a heating rate of 10 K/min are shown in Figure 2.

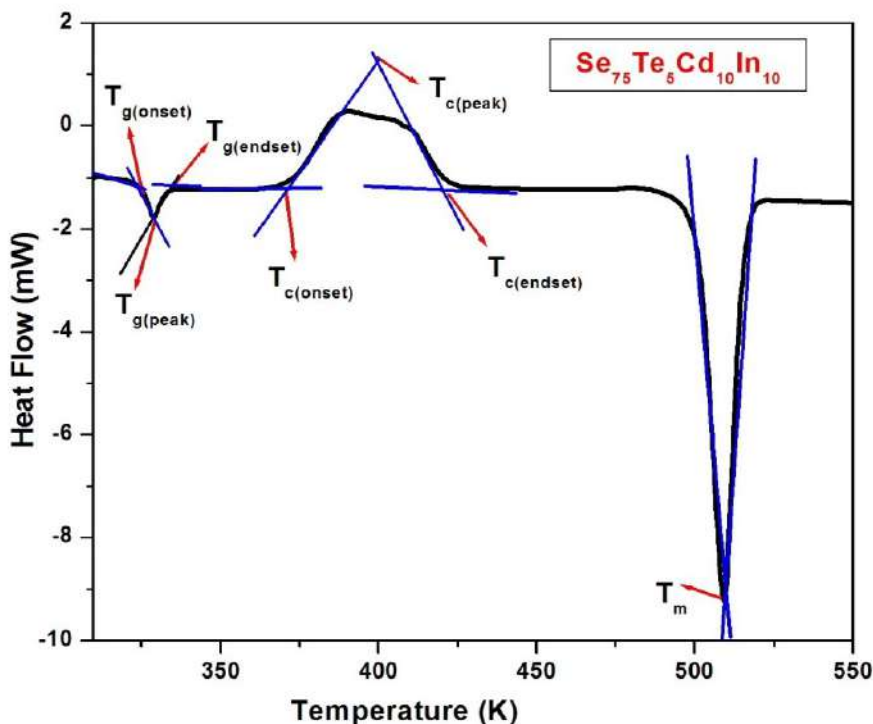


Fig. 2. DSC thermogram of the chalcogenide $\text{Se}_{75}\text{Te}_5\text{Cd}_{10}\text{In}_{10}$ glass at heating rate 10K/min.

The DSC thermogram shows both endothermic and exothermic peaks. Endothermic peaks correspond to glassy and melting regions. The exothermic peak is a representation of the onset and peak crystallization temperature. The T_g , T_c , and peak crystallization temperature T_p at a heating rate of 10 K/min are all determined using the DSC thermogram.

Thermal Stability

The relative capacity of the glass composition to maintain and conform to the amorphous state is known as glass forming ability (GFA). Models were created in the literature to calculate the GFA and the thermal stability of glasses as a bundant.²⁵ The temperature difference between glass and crystallization

temperature is used to calculate $\Delta T_{pg}=(T_p-T_g)$, a crucial indicator of glass forming ability (GFA) in amorphous materials.²⁶ Table 1 lists the measured values of ΔT_{pg} at a heating rate of 10 K/min. Crystallization starts as soon as the glass reaches the characteristic onset crystallization temperature (T_c). Because it takes less time for the amorphous to undergo crystalline transformation, the peak crystallization temperature is lower with a higher crystallization rate for a fixed heating rate.

Table 1: The Calculated values of $T_g, T_c, T_p (T_p-T_c) Fi, S$ and H_w of glassy $Se_{75}Te_{15-x}Cd_{10}In_x$ ($x = 0, 5, 10$ and 15) system

x	$\langle Z \rangle$	T_g	$T_c (K)$	$T_p (K)$	$(T_p - T_g) (K)$	Fi	S	H_w
0	2.2	326	354	382	56	28.6	4.81	0.17
5	2.25	332	383	400	68	20.1	3.48	0.20
10	2.30	323	371	396	73	22.7	5.65	0.23
15	2.35	313	363	388	75	22.2	5.97	0.24

Based on the values that define glass thermal stability, which are connected to T_g, T_c , and T_p , a number of quantitative methods have been developed to nearby on the level of thermal stability parameters in glassy alloys. In one of the earliest investigations of thermal stability in glasses, Saka and Mackenzie²⁷ employed T_g/T_m , whereas Dietzel²⁸ used $\Delta T_{pg}=T_p-T_g$. Additional later criteria included studies by Saad and Poulain,²⁹ who hypothesized a connection between these stability indicators and the stability parameter S and H_w , by

$$H_w = \frac{\Delta T_{pg}}{T_g} \quad (1)$$

$$S = \frac{(T_p - T_c)\Delta T_{pg}}{T_g} \quad (2)$$

The stability parameter S reflects the conflict to devitrification during glass manufacturing. While ΔT_{pg} slows down the nucleation process, two components (T_p-T_c) in the numerator relate to the rate at which the glassy phase undergoes devitrification transition. The graph of S with In content are shown in Figure 3, while Table 1 presents the computed values of S and H_w using equations (1) and (2) at a of 10K/min. heating rate

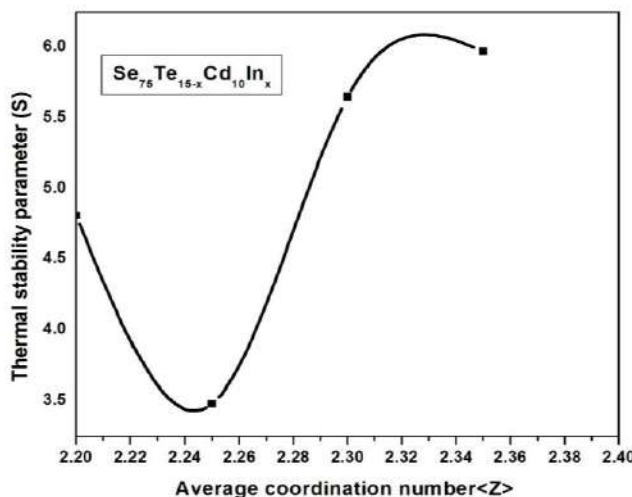


Fig. 3. Thermal Stability Parameter vs. average coordination number $\langle Z \rangle$ of glassy $\text{Se}_{75}\text{Te}_{15-x}\text{Cd}_{10}\text{In}_x$ ($0 \leq x \leq 15$) system at heating rate of 10 K/mn.

The fragility index (Fi)³⁰ measures the rate at which relaxation time decreases with increasing temperature at T_g and can be obtained by

$$F = \frac{E_g}{RT_g(\ln \beta)} \quad (3)$$

Values that shows a glass-forming liquid that is kinetically fragile, with a lower limit of $\text{Fi} \approx 16$ and an upper limit of $\text{Fi} \approx 200$.³⁰ Table 1 displays the Fi values that were calculated at a heating rate of 10 K/min. The readings vary from 20.1 to 28.6 te, indicating that the compositions under study are near strong glass-forming liquids. Strong glasses show resistance to structural degradation in the liquid state at temperatures below T_g .

The average coordination number is used to determine all of the parameters $\langle Z \rangle$. Tanaka³¹ outlines a typical approach for calculating the values $\langle Z \rangle$ for the glassy alloys under investigation. This procedure uses coordination numbers (CN) 2, 2, 4, and 3 Se, Te, Cd, and In, respectively. Therefore, the following aggregation could provide the values of $\langle Z \rangle$ for the glassy system $\text{Se}_k \text{Te}_l \text{Cd}_m \text{In}_n$ ($k+l+m+n=1$),):

All the parameters are determined using the average coordination number. A common method for determining the values for the glassy alloys being studied is described by Tanaka.³¹ The coordination numbers (CN) used in this process are 2, 2, 4 and 3 Se, Te, Cd, and In, respectively. Consequently, the values of for the glassy system $\text{Se}_k \text{Te}_l \text{Cd}_m \text{In}_n$ ($k+l+m+n=1$), might be obtained from the following aggregation:

$$\langle Z \rangle = \frac{(kZ_{Se} + lZ_{Te} + mZ_{Cd} + nZ_{In})}{(k + l + m + n)} \quad (4)$$

where k , l , m , and n are the atomic weight percentages of these elements in the glassy network, and $Z_{Se}=2$, $Z_{Te}=2$, $Z_{Cd}=4$, and $Z_{In}=3$ are their corresponding coordination numbers. For $In=0$, 5, 10, and 15, the corresponding values are 2.2, 2.25, 2.3, and 2.35.

4. Discussion

As the In content in $Se_{75}Te_{15-x}Cd_{10}In_x$ alloys increases it is obvious from Table 1, thermal stability (weighted glass) H_w , and stability parameter shows reversal trend at $x=5$ at % In (See Figure 3 and 4).

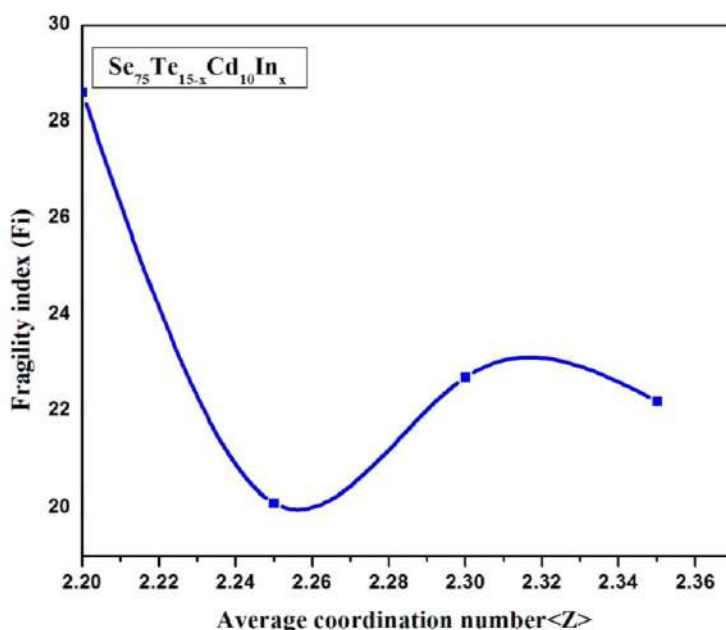


Fig. 4. Fragility Index against average coordination number $\langle Z \rangle$ of $Se_{75}Te_{15-x}Cd_{10}In_x$ ($0 \leq x \leq 15$) multi-component glasses at heating rate of 10 K/min.

The configuration dependency of these features of chalcogenide glasses has been explained by a number of theories.³²⁻⁴⁰ Among this is so-called chemically ordered network model (CONM),³²⁻³⁵ which supports the creation of heteropolar links that is, bonds between dissimilar elements over homopolar elements. According to this model, a fraction, if any, of the elements (homopolar bonds) and cross-linked structural units of the system's stable chemical compounds (heteropolar bonds) make up the glass structure. Chemical ordering at the so-called tie-line or stoichiometric compositions, where the glass structure is composed entirely of cross-linked structural units built of heteropolar bonds, causes features like extrema, variations in slope, or kinks to arise for a variety of characteristics. For tie-line compositions, the system's chemical threshold is different when the observed features have a chemical

cause.^{41,42} The other methods include constraint theory³⁵⁻³⁹ and so-called topological models, which rely on structural dimensionality considerations.⁴⁰ The characteristics of these models can be discussed using the average coordination number, which is independent of species or valence bond. By correlating the number of operational constraints to the number of degrees of freedom, the most stable glasses are determined to be close to ~ 2.4 using the constraints model.³⁴⁻³⁷ At this value of, average coordination number the glass network changes from an elastically floppy (polymeric glass) type to a rigid (amorphous solid) type. We discovered a reversal in the thermal stability parameter trend for the $\text{Se}_{75}\text{Te}_{10}\text{Cd}_{10}\text{In}_5$ alloy at $= 2.25$, which is close to the value anticipated by constraint theory-based topological models.

5. Conclusions

Thermal stability parameter, weighted glass thermal stability and fragility index have been investigated for Se-Te-Cd-In system in non-isothermal conditions. There are several kinetic parameters of crystallization that have been determined using the DSC approach. The thermal stability parameter, weighted glass thermal stability and fragility index show a trend reversal with In content at $\langle Z \rangle$ of 2.25. Observed values shows that glassy 5 at. wt.% of In, shows highest GFA, is the most stable glass of this system. This is regular with the constraint theory for chalcogenide glasses proposed by Phillips and Thorpe.

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