

phys. stat. sol. (a) **179**, 109 (2000)

Subject classification: 61.16.Ms; 61.43.Fs; 64.70.Pf; S8.12

Differential Scanning Calorimetry and X-Ray Photoelectron Spectroscopy Studies on $\text{Se}_{100-x}\text{In}_x$ System

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(Received November 22, 1999; in revised form February 25, 2000)

Chalcogenide glasses in the $\text{Se}_{100-x}\text{In}_x$ system, in the composition range $0 \leq x \leq 29$ (x in at%), were prepared from high purity Se and In. Differential scanning calorimetry results clearly indicate that the thermal stability of the glasses decreases upon increasing x . The values of the glass transition temperatures (T_g) were found to be composition independent which is interpreted by envisaging the formation of In_2Se_3 microclusters that do not contribute to the T_g values of the glasses and that these values remain to be essentially determined by that of the Se_n chains of the Se glassy matrix. The X-ray photoelectron spectroscopy results lend further support to the formation of In_2Se_3 microclusters.

1. Introduction

The investigation of electrical [1 to 12] and optical [11 to 16] properties of amorphous InSe thin films has been a subject of active research by both solid-state physicists and electronic engineers for their applications as photovoltaic [17 to 21] and memory switching [22, 23] materials.

The thermal stability of amorphous materials is an important aspect in their characterisation so as to see if they can withstand the service temperature requirement for a particular technological application. Consequent upon this we performed a differential scanning calorimetric (DSC) study on glasses belonging to the $\text{Se}_{100-x}\text{In}_x$ system. In this paper, we report and discuss the results of such a DSC study as well as the results of X-ray photoelectron spectroscopy (XPS) and density measurements performed on the $\text{Se}_{100-x}\text{In}_x$ glasses.

2. Experimental Procedures

Glass samples, within the composition range $4 \leq x \leq 29$ (x in at%), were synthesized by the conventional melt-quenching method. The method consisted of vacuum sealing the appropriate amounts (total 3 g) of high purity In and Se in evacuated (10^{-5} Torr) cylindrical (8 mm internal diameter) silica tubes. The tubes were then heated to a maximum temperature (850 °C), in steps of 100 °C, and were continuously agitated to ensure homogenization of the melt. Subsequently, the tubes were quenched to 0 °C in an ice-water mixture. To prepare pure glassy Se, the outlined procedure was used except that the sample was quenched from a lower temperature ($\cong 300$ °C) in air.

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The differential scanning calorimetry measurements (DSC) were performed using a Setaram DSC 92 instrument. The DSC curves were recorded as the temperature of the samples was increased at the constant rate of 10 °C/min. The powdered samples were sealed in aluminium pans and referenced to empty aluminium pans and the temperature was scanned from room temperature to about 275 °C. The peak of the crystallization exotherm and the minimum of the melting endotherm are taken as the crystallization (T_c) and melting (T_m) temperatures, respectively. The error in T_g , T_c and T_m , as determined from measuring the well known melting temperature of high purity In supplied with the instrument, was estimated to be less than ± 0.5 °C.

The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Perkin-Elmer CI spectrometer with monochromatized AlK_{α} radiation of 1486.6 eV. The energy spectrum of the electrons was analyzed by a hemispherical mirror analyzer operated in the fixed analyzer transmission (FAT) mode. To obtain the binding energies of Se and In relative to the Fermi level in the glasses, parts of the alloys were coated with Au so that the Au 4f_{7/2} appear at an energy of 84.0 eV. The charging of non-conducting glass samples was avoided by flooding the samples with low energy electrons ($E_k = 5$ to 10 eV, electron emission current 1 to 5 nA). Sputtering the sample surface, for a short period of time ($\cong 1$ min), with 10 mA emission current and 5 kV beam energy using an argon ion gun was enough to reduce surface contaminants to background level. High resolution scans (≤ 0.4 eV), for the glassy samples and for crystalline In₂Se₃, were obtained in the Se(3d), In(3d) and In(4d) regions of the spectrum.

The ambient macroscopic densities of the as-prepared glasses were measured by the Archimedes method using carbon tetrachloride (CCl₄) as the immersion fluid which has a density of 1.5873 g cm⁻³ at 24 °C. The densities were calculated using the formula

$$\rho_g = [w_0 / (w_0 - w_f)] \rho_f, \quad (1)$$

where w_0 , w_f and ρ_f represent the weight of the sample in air, the weight of the sample in the fluid and the density of the immersion fluid, respectively. The atomic densities of the glasses were calculated from the macroscopic densities via the relation

$$\rho_a = \rho_g N_A / \sum x_i A_i, \quad (2)$$

where x_i and A_i are the atomic concentration and the atomic weight of element i , respectively.

3. Results and Discussion

The DSC curves recorded for all the samples exhibit three consecutive phenomena. The first endothermic-like phenomenon indicates the glass transition region. The exothermic phenomenon manifests the crystallization process and the last endothermic phenomenon corresponds to the melting of the sample. A typical DSC curve for the glass with the highest In content (29 at%) is shown in Fig. 1. From the DSC curves, the values of T_g , T_c and T_m have been determined and are summarized in Table 1. The numerical values of the coefficient of the glass thermal stability (GTS) K_{gl} have been calculated for the investigated glasses according to the formula [24, 25]

$$K_{gl} = (T_c - T_g) / (T_m - T_c). \quad (3)$$

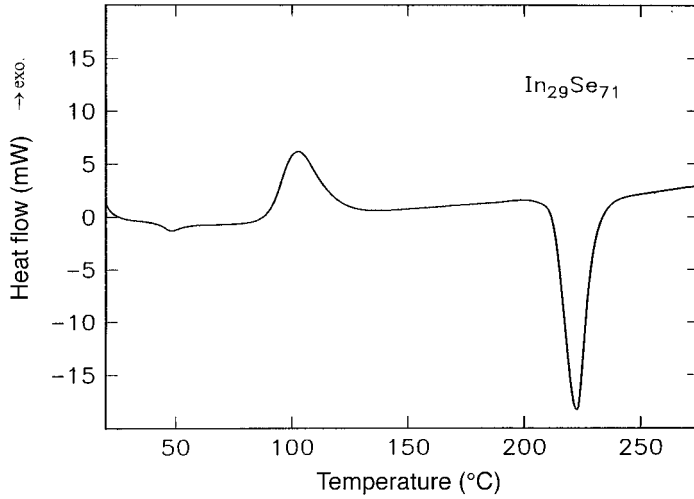


Fig. 1. A typical DSC curve obtained from the $\text{In}_{29}\text{Se}_{71}$ sample

Table 1
Thermal parameters obtained on the investigated compositions

glass composition x (at%)	T_g (°C)	T_c (°C)	T_m (°C)	$T_c - T_g$	K_{gl}
0	47.5	109.0	221.3	61.5	0.548
4	47.8	108.2	229.5	60.4	0.498
7	47.2	107.2	228.2	60.0	0.496
14	46.7	106.1	226.8	59.4	0.492
18	46.3	104.9	224.6	58.6	0.489
25	46.3	104.4	224.2	58.1	0.485
29	45.7	103.3	222.9	57.6	0.482

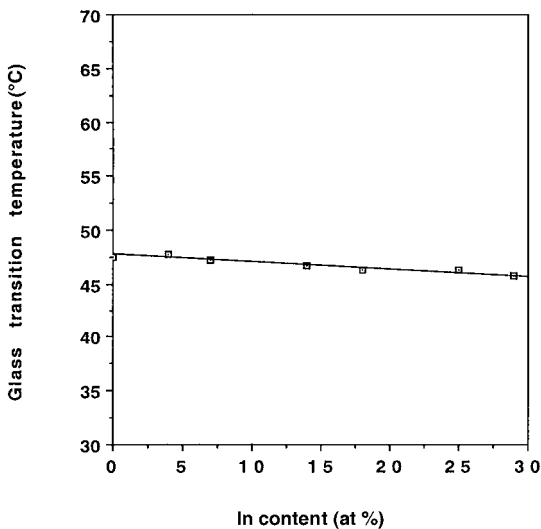


Fig. 2. Variation of the glass transition temperature with the amount of In present in the glass

The values of K_{gl} and those of the temperature interval $\Delta T = T_c - T_g$ are listed in Table 1.

According to the criterion developed by Malek [26], the value of the temperature interval $\Delta T = T_c - T_g$ may be used to assess the crystallization ability of the glass wherein a short temperature interval indicates that the glass contains structural units (s. u.) with a high crystallization tendency. It is worth noting, from the thermal data given in Table 1, that the value of $T_c - T_g$ decreases with increasing In content in the glass and that the values of K_{gl} follow the same trend. This clearly demonstrates that the increase of the In content in the glass leads to the decrease of the thermal stability of the glass, i.e. to an increase in its crystallization tendency.

In Fig. 2 we show the variation of T_g with the In content present in the glass. This figure shows that there is a slight decrease of T_g with In content. Our results on T_g and T_c agree with those reported by Abd El-Moiz et al. [27]. However, in their paper they

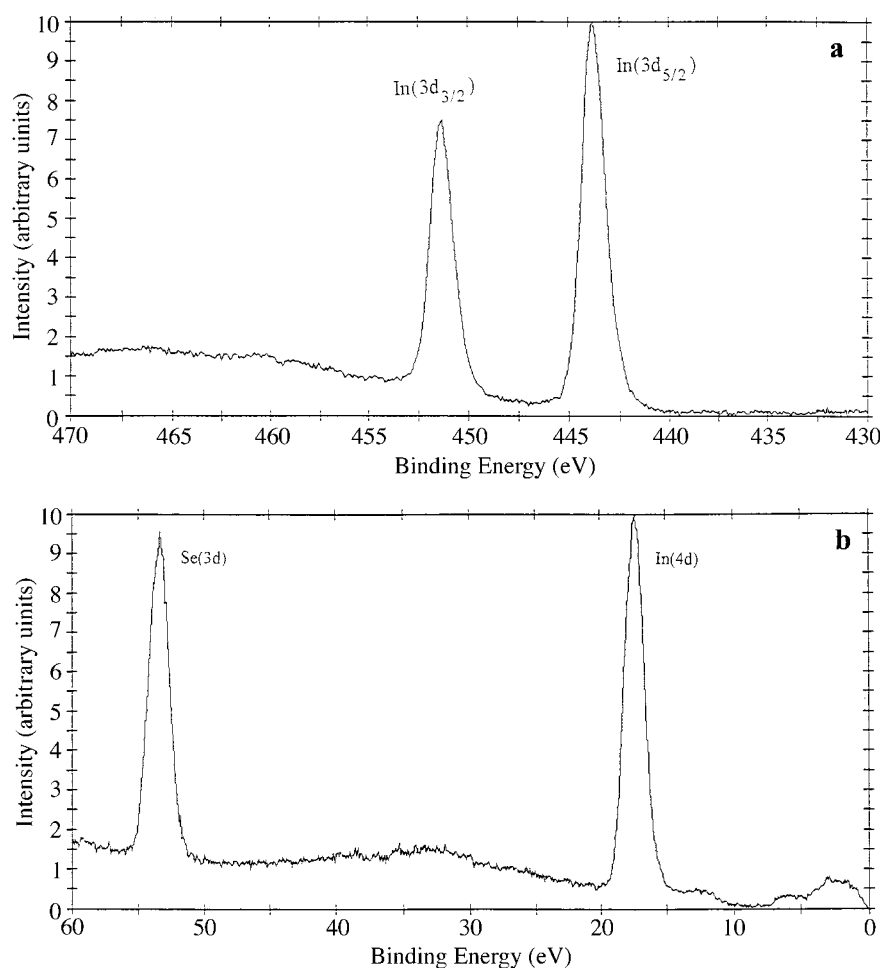


Fig. 3. XPS spectrum of a) In(3d_{3/2}, 3d_{5/2}) and b) Se(3d) and In(4d) recorded at room temperature for the In₂₉Se₇₁ sample

did not pay attention to the melting temperatures for their investigated compositions, which is considered to be a major flaw in their study. The change of T_g is discussed in the following paragraph.

The composition dependence of T_g , observed in this work for In–Se glasses, was reported for the binary Bi–Se vitreous system and attributed to the existence of structural units made of Bi_2Se_3 clusters embedded in the glassy matrix [28]. Consequently, we interpret our results regarding the composition dependence of T_g by proposing the formation of In_2Se_3 microclusters that do not contribute to T_g and that T_g of the alloys remains to be mainly governed by that of the Se chains of glassy Se. The formation of such microclusters that do not contribute to T_g values, in glasses belonging to the Ge–In–Se system, was successfully used to interpret the composition dependence of T_g for these glasses [29]. The observed composition dependence is also in accordance with the fact that there is no large difference between the bond energies of Se–Se (1.9 eV [30]) and In–Se (2.09 eV [30]). Therefore, it is not expected that the replacement of Se–Se bonds by In–Se bonds will lead to a significant change in T_g upon increasing the In content in the glass. Confirmation of the presence of In_2Se_3 microclusters on the surface of the investigated glasses comes from XPS results that will be discussed below.

Typical XPS spectra of In(3d), Se(3d) and In(4d), for the glass with the composition $\text{In}_{29}\text{Se}_{71}$, are depicted in Fig. 3a and b, respectively. The binding energies of the d-lines of the investigated glasses as well as those corresponding to crystalline In_2Se_3 and those reported by other authors are summarized in Table 2. It is seen from this table that the binding energies of Se(3d) and In(4d) experience chemical shifts upon alloying, where the Se(3d) and In(4d) shift towards lower and higher binding energies, respectively. The observed positive shift of In(4d) is indicative of its capacity to act as a donor in these glasses. This is in agreement with the reported behaviour of In in some In–Se systems [34 to 36] and also conforming with the fact that the electronegativity of In (1.7) is smaller than that of Se (2.4) [37]. The afore-mentioned shift in the binding energies of S(3d) and In(4d) is taken as an evidence for compound formation. As the binding

Table 2

Data of the binding energies (in eV) of the d-lines of the investigated samples and those reported in the literature for pure elements and $\text{In}_{50}\text{Se}_{50}$ thin film. ΔE_1 and ΔE_2 are defined in the text

sample composition (at%)	Se	In	source	ref.	In(3d _{3/2} , 3d _{5/2})	Se(3d)	In(4d)	ΔE_1	ΔE_2
100	0		glass	present work	–	55.8	–	–	–
96	4		glass	=	451.4, 443.9	53.6	17.4	36.2	390.3
93	7		glass	=	451.5, 444.1	53.5	17.4	36.1	390.6
86	14		glass	=	451.5, 444.0	53.5	17.2	36.3	390.4
82	18		glass	=	451.4, 444.0	53.4	17.3	36.1	390.6
75	25		glass	=	451.4, 443.9	53.5	17.3	36.2	390.4
71	29		glass	=	451.3, 443.8	53.4	17.3	36.1	390.4
60	40		crystal	=	451.2, 443.7	53.3	17.2	36.1	390.4
100	0		element	[31]	–	56.7	–	–	–
0	100		element	[31]	–	–	16.2	–	–
100	0		element	[32]	–	56	–	–	–
50	50		film	[33]	–	53.5	17.4	36.1	–

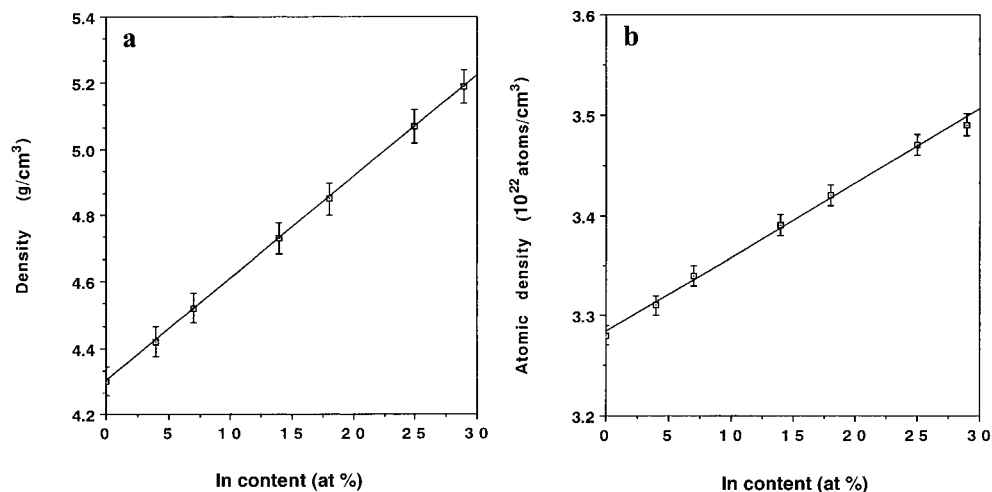


Fig. 4. Variation of the a) density and b) atomic density with the amount of In present in the glass

energies of the d-lines of Se and In and the energy differences $\Delta E_1 = [\text{Se}(3d) - \text{In}(4d)]$ and $\Delta E_2 = [\text{In}(3d_{5/2}) - \text{Se}(3d)]$ are very similar for glasses and crystalline In_2Se_3 , we ascertain that the compound formed on the surface of the glasses is In_2Se_3 in the form of microclusters.

The variation of the macroscopic density of the glass with In content is shown in Fig. 4a. The density increases linearly from 4.30 g cm^{-3} for pure Se to 5.19 g cm^{-3} for the glass containing 29 at% In. This increase of density, with increasing In content in the glass can be attributed to the larger atomic mass of In (115) as compared to that of Se (79). A similar composition dependence is exhibited by the atomic density (Fig. 4b) which is presumably due to the increase of the macroscopic density with increasing In content in the glass. The composition dependence of these two quantities indicate that the degree of packing of atoms in the glass structure increases with increasing In content.

4. Conclusions

Addition of In to Se, in varying concentrations, leads to (i) a decrease of the thermal stability, (ii) an increase in both the macroscopic density and the atomic density of the glass. The T_g values for the glasses are found to be independent of the amount of In content in the glass and this behavior is interpreted by proposing the formation of In_2Se_3 microclusters. The formation of such microclusters is corroborated by XPS results.

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