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Study of the structure of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass using the radial distribution function

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In the present work, the structure of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass has been studied using the radial distribution function (RDF). Moreover, the effect of annealing temperature on the short range order of this glass has been investigated. The results revealed that the short range order structure of the as-prepared and annealed $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass is close to a regular tetrahedron. The medium range order of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass is topology order. The topological structure of the medium range order can be described by the Phillips model. The structure of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass is stable in the annealing temperature range 324–523 K.

1. Introduction

Structural studies of chalcogenide glasses are very important for a better understanding of their physical properties [1–4].

Short and medium range order in amorphous semiconductors have been given much attention [5, 6]. Two methods have been used to investigate the short and medium range order

1. diffraction of X-rays, neutrons and electrons; and
2. analysis of the infrared absorption, infrared reflection and Raman scattering vibrational spectra.

The fullest and most direct information on the short and medium range order is provided by plotting the radial distribution function on the basis of the data obtained by diffraction of X-rays, neutrons and electrons [7].

Amorphous chalcogenide films are one of the most promising materials for optical image recording. Among the various amorphous chalcogenide films, As–Se–S–Ge film has noticeable properties, such as large and reversible changes of refractive index, light transmission between two amorphous states, heat treated and light irradiated states [8–10]. As–Se–S–Ge film has applications in the field of integrated optics, taper couplers, optical information storage and fine line lithography, etc. [8–17]. The structure of As–Se–S–Ge chalcogenide glass using Raman scattering has been investigated by Phillips *et al.* [18].

In the present work, the short and medium range order of chalcogenide glass, $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$, has been studied in terms of the radial distribution function on the basis of the data obtained by X-ray diffraction. The effect of annealing temperature on the short and medium range order of this glass has been investigated.

1.1. Theory

The interference function, $I(K)$, the reduced radial distribution function, $G(r)$, and the radial distribution function, $RDF(r)$, were calculated from measured X-ray intensities [19, 20]. Wagner [19] and Pings and Waser [20] have reviewed the theory of diffraction analysis of amorphous and liquid alloys. Measured intensities, once corrected for background, polarization and Compton modified scattering, yield the coherent intensity, $I_{coh}(K)$, where $K = (4\pi/\lambda)\sin(\theta)$ is the magnitude of the scattering factor [21–24].

The interference function $I(K)$ is related to $I_{coh}(K)$, the atomic scattering factors for electron [$f_i(K)$ for the atoms of the ith element] and the atomic concentration [X_i for the atoms of the ith element] as follows [25]

$$I(K) = [I_{coh}(K) - \langle f^2 \rangle + \langle f \rangle^2]/\langle f \rangle^2 \quad (1)$$

where $\langle f \rangle = \sum_i^n X_i \times f_i(K)$ and $\langle f^2 \rangle = \sum_i^n X_i \times f_i^2(K)$, when $\sum_i^n X_i = 1$. $I(K)$ was converted to electron units by the high angle method [24].

The reduced radial distribution function, $G(r)$, is obtained by Fourier transformation of $I(K)$ using the

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following relation [25]

$$G(r) = 4\pi r[\rho(r) - \rho_o] = 2\pi \int_0^{K_{\max}} K[I(K) - 1]\sin(Kr)\,dK \quad (2)$$

where ρ_o is the average atomic density of the alloy and $\rho(r)$ is the atomic density as a function of r. The radial distribution function, $RDF(r)$, can be written as

$$RDF(r) = 4\pi r^2\rho(r) = rG(r) + 4\pi r^2\rho_o \quad (3)$$

The average co-ordination number, N, is given by [25]

$$N = \int_{r_o}^{r'} 4\pi r^2\rho(r)\,dr \quad (4)$$

where r_o is a lower limit of r below which $\rho(r)$ is zero and r' is the first minimum of $4\pi r^2\rho(r)$.

2. Experimental procedure

High purity As, Se, S and Ge (purchased from Aldrich Co.) in appropriate at % proportions were weighed into a quartz glass ampoule (12 mm diameter). The contents of the ampoule (5 g total) were sealed in a vacuum of $\simeq 0.01$ Pa and heated in a rotary furnace at around 1300 K for 24 h. The ampoule with liquid was quenched in water at 273 K to obtain the glass. The heat treatment (annealing for 2 h) was carried out under a vacuum of $\simeq 0.01$ Pa.

X-ray investigation of the $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ powder (particle size less than 54 μm) was performed with a Phillips diffractometer (type 1710). The patterns were run with Cu as the target and graphite monochromator ($\lambda = 0.154178$ nm), at 40 kV and 30 mA, with a scanning speed of 3.6° min^{-1}. The scattering angle (2θ) had values between 4 and 110°. All the X-ray investigations were performed at ambient temperature.

3. Results

The scattered intensity has been calculated as a function of the scattering factor (K). The minimum and the maximum values of K are 2.85 and 66.8 nm^{-1}, respectively. The measured intensity has been corrected to obtain the coherent intensity, $I_{coh}(K)$. The interference function, $I(K)$, has been calculated from the coherent intensity, $I_{coh}(K)$, using Equation 1. Fig. 1 shows $I(K)$ as a function of K for the as-prepared and annealed samples (for 2 h) of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass.

To calculate $G(r)$ integration of Equation 2 was carried out numerically in the range of K values from 0 to 81.4 nm^{-1}. Reasonable extrapolation of $I(K)$ to small values of $K(< 2.85$ nm$^{-1})$ was made with a negligible effect on $G(r)$ because of the small values of $K[I(K) - 1]$ [25]. Extrapolating $I(K)$ for large K values ($K > 66.8$ nm^{-1}) produces an error on the third peak of $G(r)$. This error is irrelevant as this study is only concerned with the first two peaks of $G(r)$ [26, 27]. Fig. 2 shows $G(r)$ versus r for the as-prepared and annealed samples (for 2 h) of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass.

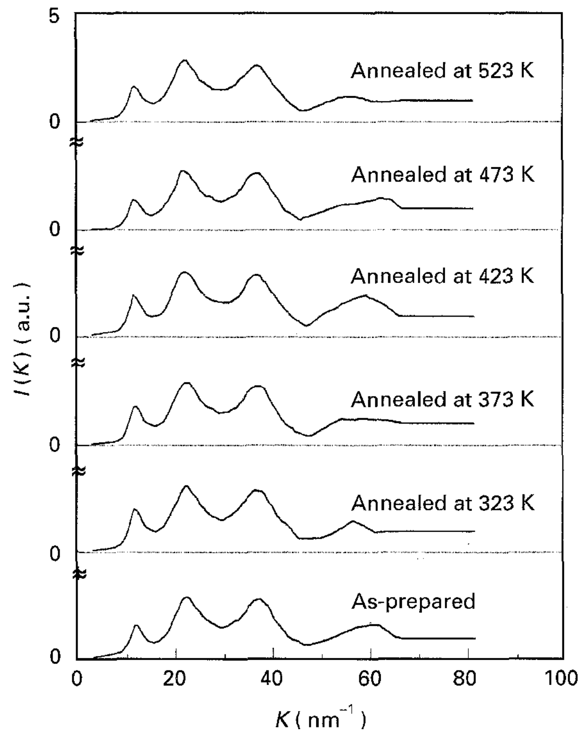

Figure 1 The interference function, $I(K)$, versus K of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass at different annealing temperatures.

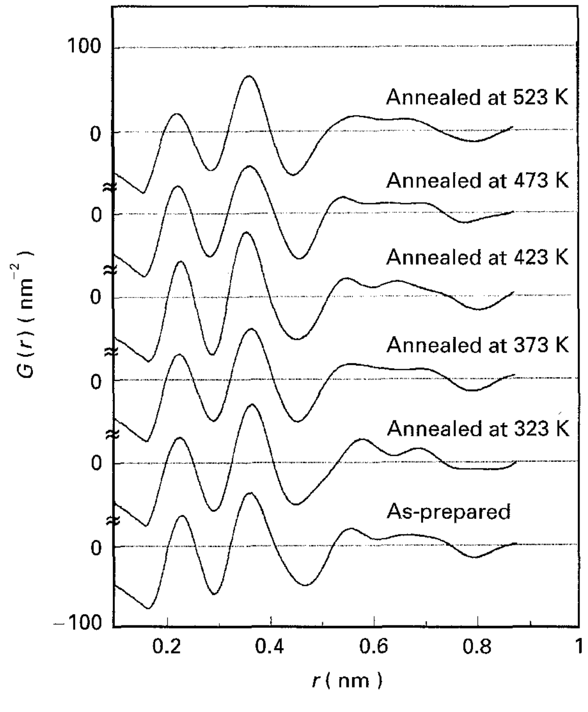

Figure 2 The reduced radial distribution function, $G(r)$, versus r of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass at different annealing temperatures.

The radial distribution function, $RDF(r)$, for as-prepared and annealed samples, is calculated from the $G(r)$ values using Equation 3. The value of ρ_o used in this calculation is 37.1 at nm^{-3}. Fig. 3 shows $RDF(r)$ as a function of r for as-prepared and annealed samples (for 2 h) of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass.

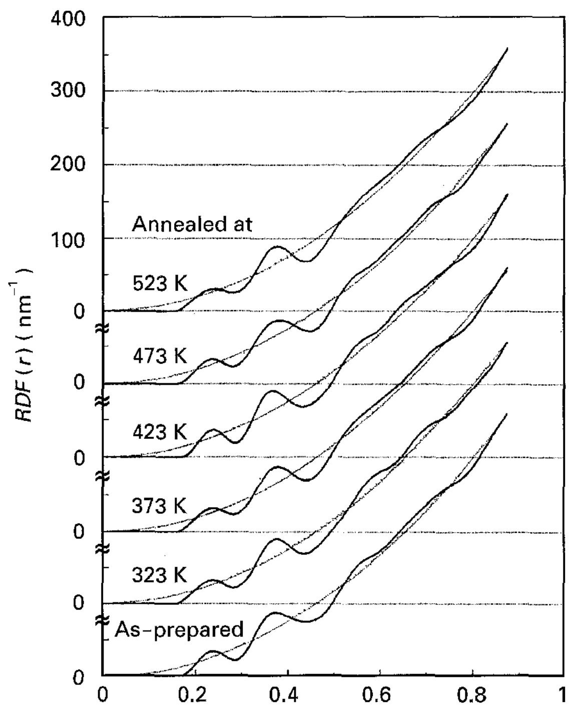

Figure 3 The radial distribution function, *RDF*(*r*), versus *r* of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass at different annealing temperatures.

4. Discussion

The X-ray diffraction of the as-prepared and annealed samples of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass proved that the as-prepared and the heat treated samples (annealed for 2 h) are in the amorphous state over the temperature range of this study. This result is in good agreement with Oe *et al.* [28].

4.1. Short range order

Fig. 2 shows the variation of the reduced radial distribution function, $G(r)$, with r for as-prepared and annealed samples of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass. The position of the first peaks, r_1, the position of the second peaks, r_2, and the (r_2/r_1) ratios deduced from Fig. 2 are listed in Table I. The position of the first peak, r_1, gives a value for the nearest neighbour bond length and the position of the second peak, r_2, gives a value for the next-nearest neighbour distance [29, 30]. The value of (r_2/r_1) ratio is equal to the average value of (c/a) ratio in the tetrahedron structure [31]. For as-prepared and all annealed samples, the values of (r_2/r_1) ratios are approximately constant. The average value of (r_2/r_1) ratios is 1.60 ± 0.02 which is the typical value of regular tetrahedron structure.

The bond angle, Θ, can be calculated as [29, 30]

$$\Theta = 2\sin^{-1}\left(\frac{r_2}{2r_1}\right) \qquad (5)$$

The bond angle values for the as-prepared and all annealed samples are listed in Table I. No significant changes in the bond angles are observed. The average value of the bond angle is 105.9 ± 2.2° which is close to the value of bond angle for tetrahedral co-ordination. The values of the full width at half maximum of the first peaks ($FWHM_1$) and that of the second peaks ($FWHM_2$) are listed in Table I. The average value of $FWHM_2$ (0.075 ± 0.003 nm) is greater than $FWHM_1$ (0.070 ± 0.005 nm). This can be attributed to the thermal vibration of the atoms and the presence of static disorder in the bond length [29, 30].

From Fig. 3, the average co-ordination numbers of the first peak, N_1, and the second peak, N_2, are listed in Table I. The annealing did not have any significant influence on N_1 and N_2. The average values of N_1 and N_2 are 2.70 ± 0.12 and 6.10 ± 0.36, respectively. The average co-ordination number of the second peak is greater than that of the first peak.

The annealing temperature did not have any significant effect on the above parameters. This means that the atom distribution remains a regular tetrahedral structure in this range of annealing temperatures. These results are in good agreement with previous results, which indicate that the As–Se–S–Ge chalcogenide glass remains amorphous in this temperature range [32].

4.2. The medium range order

In Fig. 1 it is indicated that, for as-prepared and all annealed samples, the interference function, $I(K)$, has prepeaks at about $K \approx 12\ \mathrm{nm}^{-1}$. The presence of the prepeak is the strongest indication for the existence of clusters of medium range order. The origin of this prepeak is due to the fact that many materials have crystalline polyamorphs which have a layer structure with interlayer separation of the order 0.4–0.6 nm. Diffraction from the layers produces the prepeak. The

TABLE I The effect of the annealing temperature on the parameters of $G(r)$ and $RDF(r)$ for $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ glass

	As-pre	Annealing temperature (K)					
		324	373	423	473	523	Average
r_1, nm	0.230	0.228	0.228	0.234	0.228	0.228	0.229 ± 0.003
r_2, nm	0.362	0.366	0.368	0.362	0.366	0.368	0.366 ± 0.002
Θ, deg	103.8	108.1	107.7	103.3	104.6	107.6	106.3 ± 2.2
$FWHM_1$, nm	0.067	0.076	0.071	0.064	0.067	0.077	0.071 ± 0.006
$FWHM_2$, nm	0.071	0.073	0.078	0.073	0.080	0.074	0.076 ± 0.003
N_1	2.73	2.69	2.74	2.54	2.61	2.91	2.70 ± 0.14
N_2	6.10	6.14	6.05	5.94	6.76	5.98	6.37 ± 0.44

TABLE II The effect of annealing temperature on the parameters of the interference function for $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ glass

	As-pre	Annealing temperature (K)					
		324	373	423	473	523	Average
K_{pre}, nm^{-1}	11.89	11.89	11.89	11.89	11.89	12.18	11.95 $\pm$ 0.13
$I(K)_{pre}$, a.u.[a]	1.637	2.118	1.779	2.057	1.467	1.639	1.812 $\pm$ 0.275
r_{pre}, nm	0.528	0.528	0.528	0.528	0.528	0.516	0.526 $\pm$ 0.005
K_{fp}, nm^{-1}	22.17	22.44	22.44	22.44	21.90	22.44	22.32 $\pm$ 0.24
$I(K)_{fp}$, a.u.	2.917	3.141	2.898	3.083	2.830	2.894	2.969 $\pm$ 0.135
r_{fp}, nm	0.283	0.280	0.280	0.280	0.287	0.280	0.281 $\pm$ 0.003
$FWHM_{pre}$, nm^{-1}	2.702	2.723	2.755	2.616	2.556	3.125	2.755 $\pm$ 0.221
R, nm	2.323	2.305	2.278	2.400	2.456	2.011	2.290 $\pm$ 0.172

[a] a.u., arbitrary units.

position of the prepeak corresponds well to that of the interlayer Bragg peak seen in crystalline material [33]. Its position in real space, r_{pre}, ($r_{pre} = 2\pi/K_{pre}$) is listed in Table II. These values of r_{pre} are in the range of medium range order (0.4–0.6 nm) [29,33]. r_{pre} is called the interlayer separation [29] or cluster radius [34]. The appearance of medium range order in this glass can be attributed to the germanium atom [20,35–39] or to the arsenic atom [29], where the prepeak has been observed in germanium chalcogenide glasses (Ge–S and Ge–Se systems) [29,35–39] and in arsenic chalcogenide glasses (As–S and As–Se systems) [29].

The position of the prepeaks did not change with annealing, except for the sample annealed at 523 K. The value of r_{pre} decreases slightly with respect to the other samples. This means that the intercluster distance did not change by annealing at temperatures up to 473 K, and annealing at 523 K causes a slight decrease in the intercluster distance. This slight decrease of the cluster size is expected due to the phase change of this glass at this temperature [32]. The As–Se–S–Ge glass is amorphous and has a glass transition temperature at about 500 K [32]. Above this temperature (about 530 K) the structure of this glass transfers from one amorphous phase to another more stable than the first [32]. The stability of r_{pre} means that no crystallization takes place in this range of temperatures [40,41]. Therefore, it is expected that the intercluster distance will remain constant or decrease. The $I(K) - K$ relation shows that broadening of the prepeaks is unchanged by increasing the annealing temperature up to 473 K. This is conclusive evidence that the prepeak is not associated with microcrystallites [42]. For the sample annealed at 523 K, increase in the prepeak broadening can be attributed to a decrease in the intercluster distance.

Mangin *et al.* [36] and Laridjani *et al.* [43] have demonstrated that the prepeak is the innate property of a layer structure and therefore topological ordering also causes the occurrence of the prepeak in the diffraction patterns of chalcogenide glasses [44]. The results of this work show that the topological order did not change in the range of temperature used, except at a temperature above 520 K (the second amorphous phase of As–Se–S–Ge glass [32]).

The origin of the prepeak must be attributed to the presence of large molecular clusters with a centre-to-centre spacing, r_c, ≈ 0.5 nm. If these clusters are quasiplanar a correlation length, R, normal to planes can be estimated from the full width at the half maximum of the prepeak ($FWHM_{pre}$) [42] as

$$R = 2\pi/FWHM_{pre} \qquad (6)$$

The values of $FWHM_{pre}$ and R are listed in Table II. It is clear that, for the first amorphous phase (the as-prepared and annealed samples up to 473 K for 2 h), the correlation length is approximately constant and has an average value equal to 2.352 $\pm$ 0.066. For the second amorphous phase (the sample annealed at 523 K for 2 h) the correlation length decreased by about 15% of the average value of the first amorphous phase.

Generally, the structural stability of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass with annealing can be interpreted using the Phillips proposal for arsenic sulphide [44–46]. When heated or annealed, the arsenic sulphide glasses are more resistant to crystallization. Phillips [44–46] proposed that there are stocks of layers present in the glass, which are not microcrystalline. He suggests that this atomic arrangement has a minimal strain energy [46].

5. Conclusions

From the (r_2/r_1) ratio (1.60 $\pm$ 0.02) and the bond angle (105.9 $\pm$ 2.2°) the short range order structure of the $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass is regular tetrahedron structure.

From the appearance of the prepeaks in the interference functions, the atomic distribution of the as-prepared and annealed $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ glass has a medium range order. The medium range order of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass is topological. This is described by the Phillips model.

The glass structure of $As_{0.3}Se_{0.2}S_{0.4}Ge_{0.1}$ chalcogenide glass is stable in the annealing temperature range used.

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