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STUDY OF FIRST SHARP DIFFRACTION PEAK IN As_2S_3 GLASSES BY X-RAY POWDER DIFFRACTION METHOD

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Two As_2S_3 glasses denoted glass I and glass II obtained respectively by slow and rapid quenching methods have been studied by means of X-ray powder diffraction method. The X-ray diffraction (XRD) patterns of these glasses indicate three broad diffraction peaks located at different diffraction angles 2θ between 15°-22°, 30°-38° and 50°-60°. The presence of the first broad peak called first sharp diffraction peak (FSDP) in the X-ray diffraction patterns of glass I and glass II is an indication of the existence of the medium-range order (MRO) or intermediate range order (IRO) in these glasses. MRO can be defined as the structural arrangement in non-crystalline solids beyond the first coordination shell. The position of FSDP (2θ) and its full width at half maximum (FWHM), obtained after fitting the XRD of the glasses, have been used to determine numerically the other parameters of FSDP such as the repetitive characteristic distance (R_1) and the structural correlation length (L_1). Effect of the quenching method on the above parameters has been also discussed.

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1. Introduction

In diffraction patterns obtained from amorphous solids, a narrow pre-peak known as the first sharp diffraction peak (FSDP) exists and it appears without regard for the dimensionality of the glass [1, 2]. A. A. Vaipolin and E. A. Pora-Koshits [1] have reported firstly the FSDP in X-ray scattering patterns of As_2S_3, As_2Se_3 and As_2Te_3 glasses. The formation of clusters [3-10], the presence of layers [11-13] and a chemical bond approach [14-16], have been proposed for the understanding of the structural origin of FSDP in the study of amorphous structures. According to [17], the FSDP can arise for a variety of structural reasons in amorphous materials with very different structures. Its (FSDP) origin in covalent glasses has frequently been ascribed to some form of structural element at the intermediate range length (5-50 Å) having a direct crystalline counterpart [18]. The structural element at the intermediate-range length scale that gives rise to the FSDP is the same in both the liquid and the glass [18].

The aim of this paper is to study by using X-ray powder diffraction method, the first sharp diffraction peak (FSDP) of two As_2S_3 glasses prepared by slow and rapid quenching methods. This will enable us to compare the FSDP's parameters obtained from these materials. Comparison of our results with those of As_2S_3 glasses in the literature concerning the FSDP's parameters will also be done.

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2. Glasses preparation

Two glasses of As_2S_3 or $As_{40}S_{60}$ were prepared by direct synthesis from pure starting elements such as As and S. Quartz ampoules were filled with the mixed elements and then evacuated to ~ 10^{-3} torr, sealed and heated to 900°C at the rate of 1°C/min. The tubes were held at this temperature for 24 hours and then quenched using different methods: one of the samples is slowly quenched in the heating apparatus (glass I) and the other is rapidly quenched in ice-water (glass II). Powder X-Ray Diffraction (XRD) of the samples was recorded at room temperature using a Philips PW 1050 X-ray diffractometer working at 40 kV and 20 mA with Cu-Kα radiation (λ=1.54185Å). The range of diffraction angles 2θ is between 10 and 60°. The scanning in 2θ steps is 0.04° and the integration time is 17.5 s/point.

The XRD patterns of the glasses were analysed by fitting them to lorentzian functions using the second derivative method of Peak Fit programs in order to obtain the parameters of each diffraction peak such as the area, the amplitude, the position (2θ) and the full width at half maximum (FWHM). This can enable us to see the observed changes in the FSDP with preparation methods.

3. Results

Fig. 1 indicates the angular distributions of X-ray diffraction intensity for glass I (obtained by slow quenching in the heating apparatus) and glass II (obtained by rapid quenching in ice water) in the range of diffraction angles 2θ from 10 to 60° (θ is the Bragg angle).

It can be seen that the general shape of these patterns is the same for As_2S_3 glasses obtained by different quenching methods. In the range of X-ray diffraction patterns (from 10° to 60°), the glasses look similar because they exhibit three halo (or broad) diffraction peaks located at different values of 2θ between 15°-22°, 30°-38° and 50°-60°.

The X-ray diffraction (XRD) patterns of the glasses indicate that these materials contain no diffraction peaks of As_2O_3 crystals observed at 2θ around 13°, 26° and 39° according [19]. Table 1 shows results obtained after fitting the XRD of glass I and glass II.

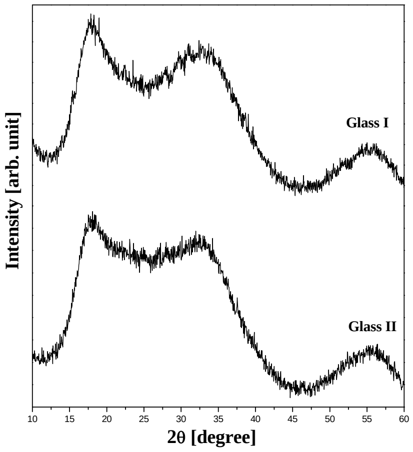

Figure 1 : X-Ray diffraction patterns of slowly-cooled (Glass I) and rapidly-quenched in ice water (Glass II) As_2S_3 glasses

Table 1: Number of the peak, area, amplitude, position (2θ) and full width at half maximum (FWHM) of the peaks obtained from XRD for glass I and glass II.

Glass I, Sm%=19.80, R^2=0.9397					Glass II, Sm%=19.80, R^2=0.9356				
Peak	Area (a.u)	Amplitude (a.u)	2θ (°)	FWHM (°)	Peak	Area (a.u)	Amplitude (a.u)	2θ (°)	FWHM (°)
1	**11390**	**1515.843**	**17.96**	**4.783**	**1**	**10870**	**1570.888**	**17.84**	**4.406**
2	6680.68	889.165	25.16	4.783	2	8756.02	1265.275	24.88	4.406
3	**10720**	**1427.228**	**33.80**	**4.783**	**3**	**10040**	**1450.155**	**33.56**	**4.406**
4	**4582.72**	**609.937**	**55.60**	**4.783**	4	2210.65	319.447	40.56	4.406
					5	**3563.61**	**514.953**	**55.72**	**4.406**

The studied glasses are smoothed (Sm %) and R^2 is the correlation coefficient between the experimental XRD and that obtained after fitting. The bold type numbers in the above table correspond to the three halo (or broad) diffraction peaks located at different values of 2θ between 15°-22°, 30°-38° and 50°-60° as shown in figure 1.

Table 1 indicates that XRD patterns of glass I and glass II are respectively composed of four and five diffusion peaks. From the above table, shoulders are found at 2θ around 25,16° for glass I and 24,88° for glass II. In the reciprocal space, the positions of these shoulders appear at 1,77 $Å^{-1}$ and 1,75 $Å^{-1}$ respectively for glass I and glass II. Even if 1,77 $Å^{-1}$ is slightly higher than 1,75 $Å^{-1}$, it is possible to suggest that these shoulders appear at the same position. The above values are in agreement with the study on As_2S_3 made by [20] who observed a position of a shoulder at 1,70 $Å^{-1}$. For glass II, another shoulder appears at 2θ equal to 40,56°. This shoulder is absent on the XRD pattern of glass I.

Results of important three broad peaks observed in XRD patterns (figure 1) presented in table 2 indicate the decreasing of the area and the amplitude of the peaks and the increasing of their position (2θ).

Table 2: Area, amplitude, position 2θ and full width at half maximum FWHM corresponding to the three broad peaks for glass I and glass II.

Glasses	Peaks	Area (a.u)	Amplitude (a.u)	2θ(°)	FWHM (°)
Glass I	1	11390	1515.843	17.96	4.783
	3	10720	1427.228	33.80	4.783
	4	4582.72	609.937	55.60	4.783
Glass II	1	10870	1570.888	17.84	4.406
	3	10040	1450.155	33.56	4.406
	5	3563.61	514.953	55.72	4.406

The area peak values of glass I are higher than those of glass II. The amplitude values and those of the position of the first and third diffraction peaks of glass I are lower than those of glass II. The contrary behaviour is observed concerning the amplitude and the position in the case of the fourth (glass I) and the fifth (glass II) broad diffraction peaks. The FWHM of the peaks remains the same for all the peaks of each glass and its values are equal to 4.783 and 4.406° respectively for glass I and glass II.

Table 3 shows the different values of the three broad diffraction peaks position in the reciprocal space of As_2S_3 glass obtained by air quenching method from reference [20] and our results. The position of the broad peaks (Q_i) in the reciprocal space presented in table 3 has been calculated by using the following formulae $Q_i=(4\pi/\lambda \sin \theta_i)$ where Q_i is the position of the ith broad peak.

Table 3 : Values of the first, second and third broad peaks' position (Q_1, Q_2 and Q_3) of As_2S_3 glasses obtained by different quenching methods.

Materials	Q_1 (Å)$^{-1}$	Q_2 (Å)$^{-1}$	Q_3 (Å)$^{-1}$	References
As_2S_3 glass	1.220	2.290	3.780	[20]
Glass I	1.281	2.315	3.797	This work
Glass II	1.290	2.284	3.814	This work

To make comparison between our results and those of the literature, the position of the third broad peaks in the XRD patterns of glass I and glass II can be associated to the second broad peaks (Q_2). The fourth broad peak of glass I and the fifth broad peak of glass II can be also associated to the third broad peak (Q_3). Thus, slight differences can be observed when comparison is made between the positions of the first (Q_1), second (Q_2) and third (Q_3) of the glasses mentioned in table 3. This can enable us to conclude that, each broad diffraction peak appears at the same value of the position in the three cases. The quenching methods do not modify highly the position of the three broad peaks of the obtained As_2S_3 materials. The very small divergence observed in the position of the peaks can be attributed to possible differences in the sample preparation, its technique and XRD pattern measuring accuracy.

The first broad diffraction peak observed at different values of 2θ between 15° and 22° on XRD patterns of glass I and glass II (figure 1) is called the first sharp diffraction peak (FSDP). Its presence has been mentioned in several papers concerning chalcogenide [21-26], oxide [27-31], silicate [32] and metallic [33-35] glasses. FSDP's values such as 2θ and FWHM deduced from the XRD patterns of glass I and glass II have been used to calculate numerically the other parameters of FSDP:

- R_1 (a repetitive characteristic distance), related to the structural unit size corresponding to FSDP or to the distance between the layers that may also be formed [11-13] or to the quasi-periodic atomic density fluctuations [14-16], can be determined by the position of FSDP (Q_1),
- L_1 (the structural correlation length) is determined using the width (FWHM) of FSDP.

The estimation of Q_1, R_1, ΔQ_1 and L_1 has been made using the below expressions:

$$Q_1=(4\pi/\lambda)\sin\theta \tag{1}$$
$$R_1=2\pi/Q_1 \tag{2}$$
$$\Delta Q_1=(4\pi/\lambda)\sin(FWHM/2) \tag{3}$$
$$L_1=2\pi/\Delta Q_1 \tag{4}$$

Note that, Q_1 and ΔQ_1 are respectively the position and the width of FSDP in the reciprocal space. L_1, being also the scale of the medium range order like R_1, is related to some characteristic distance between the underlying structural units which produce the FSDP in the diffraction pattern [36, 37] or the size of the stable cluster structure [34, 38] or the correlation length over which the quasi-periodic real space density fluctuations are maintained [25]. According to [34], the correlation length is an important parameter used to evaluate the degree of microstructure ordering of the chemical short-range order structure (or cluster).

The values of the parameters 2θ, FWHM, Q_1, ΔQ_1, R_1 and L_1 for glass I and glass II are summarized in table 4 which also indicates for the above materials, the ratio values on the one hand between L_1 and R_1 and on the other hand between ΔQ_1 and Q_1.

Table 4: Parameters 2θ, FWHM, Q_1, ΔQ_1, R_1 and L_1 of the FSDP and the ratio values of L_1/R_1 and $\Delta Q_1/Q_1$ of glass I and glass II.

Glasses	2θ°	FWHM°	Q_1(Å)$^{-1}$	ΔQ_1(Å)$^{-1}$	R_1(Å)	L_1(Å)	L_1/R_1	$\Delta Q_1/Q_1$
Glass I	17.96	4.783	1.272	0.340	4.939	18.480	3.742	0.267
Glass II	17.84	4.406	1.264	0.313	4.971	20.074	4.038	0.247

From the above table, several comments can be done. The position (2θ or Q_l) and FWHM or ΔQ_l of glass I are higher than those of glass II. They also induce small values of R_l and L_l because R_l and L_l of glass I are lower than those of glass II. The same behaviour is also observed in the case of the ratio L_l/R_l. But concerning the ratio $\Delta Q_l/Q_l$, the opposite behaviour can be observed because $\Delta Q_l/Q_l$ of glass II is lower than that of glass I. In order words, all parameters mentioned in table 4 show a clear dependence of quenching methods. The ratio L_l/R_l is equivalent to the ratio $Q_l/\Delta Q_l$ [37]. It is shown that the width of the peak related to medium order depends on its position and, according to [37], the ratio $\Delta Q_l/Q_l$ for the FSDP for various glasses varies from 0.2 to 0.3. The data of ratio $\Delta Q_l/Q_l$ being equal to 0.267 and 0.247 respectively for glass I and glass II belong to the range 0.2–0.3.

Table 5 indicates the parameters of FSDP deduced from XRD patterns of As_2S_3 glasses and films obtained by different authors in the literature. It can be seen that the FSDP's parameters are dependent on the method used to prepare As_2S_3 glasses and films and also on the experimental technique used to obtain the X-ray diffraction patterns of the materials. These parameters seem to be different when comparison is made between them. In other words, FSDP's parameters show a clear dependence of the method used to obtain the materials and the experimental technique used to study or to have information concerning the FSDP's parameters.

Table 5: FSDP's parameters of As_2S_3 materials obtained by using different methods.

Synthesis	Exp. means	2θ°	FWHM°	Q_l(Å)	ΔQ_l(Å)	R_l(Å)	L_l(Å)	Ref.
Q.A.R.T	N.D	---	---	1.220	0.310	5.15	20.27	[20]
Q.W	P.D	17.84	3.880	1.264	0.276	4.97	22.80	[39]
A.F.P.T.E	X.R.D.A	17.05	4.205	1.208	0.299	5.20	21.00	[40]
A.F.P.I.P.S	X.R.D.A	16.72	5.189	1.185	0.369	5.30	17.00	[40]
S.Q.A	X.R.P.D	17.96	4.783	1.272	0.339	4.939	18.534	This work
R.Q.I.W	X.R.P.D	17.84	4.406	1.264	0.313	4.971	20.074	This work

***Q.A.R.T**: Quenching in air at room temperature; **N.D**: Neutron diffraction; **Q.W**: Quenching in water; **P.D**: Powder diffractometer; **A.F.P.T.E**: Amorphous films prepared by thermal evaporation; **A.F.P.I.P.S**: Amorphous films prepared by ion-plasma sputtering; **X.R.D.A**: X-ray diffraction analysis; **S.Q.A**: Slow Quenching in the heating apparatus; **R.Q.I.W:** Rapid quenching in ice-water; **X.R.P.D**:X-ray powder diffraction.*

This is in agreement with M. Aniya and F. Shimojo [41] who stipulated that the specific interatomic correlations that originate the observed FSDP depend on the glassy system under consideration and on the technique to measure it.

Note that, FSDP's values such as Q_l and R_l belong respectively to 1.185-1.3 $Å^{-1}$ and 4.80-5.3 Å ranges (table 5). This is in agreement with [42] who show that FSDP is situated at low structure factor values (1.0-1.5 $Å^{-1}$) and arises probably from correlation at distances of 4.5-6.0 Å rather than from simple nearest or next nearest neighbours. The position of FSDP of As_2S_3 (glass II) prepared in our case by rapid quenching method in ice water found around 2θ=17.84°, is in a good agreement with that of As_2S_3 in the literature data [39]. The average value of its position in the reciprocal space equal to 1.264 $Å^{-1}$, is also in agreement with that obtained by [39] from X-ray diffraction experiments for the liquid and amorphous arsenic chalcogenide. FWHM of the FSDP for glass II being equal to 4.406° or ΔQ_l=0.313 $Å^{-1}$ is higher than that of As_2S_3 glass obtained by rapid quenching in water method [20] where the value of this characteristic is equal to 3.88° or ΔQ_l=0.276 $Å^{-1}$. The repetitive distance R_l and structural correlation length L_l for glass II are 4.971 Å (equal to that of As_2S_3 obtained by quenching in water) and 20.074 Å (lower than that of As_2S_3 obtained by quenching in water).

In order to reflect the proportion of the structure corresponding to the first diffraction peak in the matrix for $Al_{90-x}Ni_{10}Ce_x$ (x=3, 5, 6, 8) glasses, the ratio of this first diffraction peak area to the total area of the diffraction peaks in X-ray intensity curve, S_{FSDP}/S_{Total} has been calculated by L.

Hu et al [34]. Following the idea of the above authors and taking into account the area values of all peaks in table 1 for the two glasses, the calculated ratio or the proportion of the structure corresponding to each broad peak in the matrix of glass I and glass II is shown in table 6.

Table 6: Area, the ratio ($S_{ith\ peak}/S_{Total}$) and the amplitude of the structure corresponding to the three broad peaks for glass I and glass II

Glasses	Peaks	Area (a.u)	$S_{ith\ peak}/S_{Total}$	Amplitude (a.u)
Glass I	1	11390	0.341	1515.843
	3	10720	0.321	1427.228
	4	4582.72	0.137	609.937
Glass II	1	10870	0.307	1570.888
	3	10040	0.283	1450.155
	5	3563.61	0.100	514.953

It indicates that the ratio decreases like the area of the peaks. The two characteristics and the amplitude have the same trend as indicated in table 6. It can be noted that, the ratio or the population of the structure corresponding to each broad peak in the matrix of glass II is lower than that of glass I. But among the three broad peaks, the proportion of the structure corresponding to the FSDP has the higher value in each case of As_2S_3 glasses. This can enable us to suggest that, the production of FSDP by cooling slowly the melt needs higher population than the case of cooling rapidly the melt.

4. Discussions

The broad diffraction peaks observed in all of the diffraction patterns (figure 1) indicate the total vitrification of glass I and glass II. The quenching methods used in our case can produce materials with the same chemical composition in the same identical state. The location of the three broad diffusion peaks at 2θ values between 15-22°, 30-38° and 50-60° can mean that the basic structural units are similar and they are preserved in the two glasses obtained by different quenching methods. The absence of diffraction peaks of As_2O_3 crystals observed at 2θ around 13°, 26° and 39° according [19], indicates that the glasses' surface is not contaminated by oxygen.

The presence of the first peak among the three broad diffraction peaks observed on the XRD patterns of glass I and glass II called FSDP is an indication of the existence of intermediate range order (IRO) [42]. IRO is also called medium range order (MRO) and can be defined as an order extending beyond the length scale of nearest and next-nearest neighbour distances or a structural arrangement in chalcogenides beyond the first coordination shell [22]. In other words, FSDP is caused by the medium-order in the glass [27] and its presence also corresponds to a compound-forming behaviour [43], or can be attributed to a cluster structure made up of unlike atoms [44]. The above suggestions made by these different authors enable us to consider the parameter R_1 as the distance between the layers that may also be formed [11-13] or to the quasi-periodic atomic density fluctuations [14-16]. The parameter L_1 is considered as the size of the stable cluster structures [34, 38] or the correlation length over which the quasi-periodic real space density fluctuations are maintained [25]. The repetitive characteristic distance R_1 of FSDP for glass I is equal to 4.939 Å and that of glass II is also equal to 4.971 Å. This implies that the quasi-periodicity (R_1) increases slightly from the slow quenching method to the rapid quenching one. Even if the rapid quenching method modifies slightly this parameter, it's possible to suggest that the FSDP appears at the same position in the real space because the obtained values of R_1 in the two cases are nearly the same. The parameter L_1 which is considered as the size of structures responsible of FSDP (or the correlation length over which the quasi-periodic real space density fluctuations are maintained) for glass I (18.480 Å) is lower than that of glass II (20.074 Å). L_1 increases from slow quenching method to the rapid quenching one. So the above values of L_1 are influenced by the quenching method used to obtain the glasses. Among the studied glasses, glass I has a stronger disorder because its FWHM value equal to 4.783° is greater than that of glass II which is equal to 4.406°. According to S. Mamedova et al [45], the width of the FSDP gives information about the distribution of structural fragments. The behaviour corresponding to a compound formation can be seen in table 1 where the amplitude or intensity of FSDP in glass II (1570.888) is slightly higher than that of glass I (1515.843). As the difference between the two values is not very high (55.045), we can suggest that the compound formation in the two glasses obtained by two quenching methods is approximately the same. In the As_2S_3 or $As_{40}S_{60}$ glasses (or glass I and glass II) obtained by different quenching methods, there are three independent pair correlations (As-As, As-S, S-S). The atomic concentration of As and S being respectively equal to 40 and 60 percent, the above three correlations can exist in glass I and glass II. Since the FSDP corresponds to strong interaction between unlike atoms [44], we can suggest that FSDP in the above glasses can be attributed to As-S correlations. So the preparation of As_2S_3 glass by using the rapid quenching method can increase the intensity of FSDP. But the contrary behaviour is observed in the case of slow quenching method. The rapid quenching method can improve the interaction between unlike atoms.

The ratio value of S_{FSDP}/S_{Total} (table 6) of glass I being higher than that of glass II indicates that rapid quenching method produces more structural units forming the FSDP than the slow quenching method. The same behaviour is observed for the other broad diffraction peaks (table 6). The values of $S_{ith\ peak}/S_{Total}$ (table 6) decrease with the area and the amplitude of the broad peaks in each case of As_2S_3 glasses prepared by different quenching methods. As the three characteristics have the same trend, the ratio $S_{ith\ peak}/S_{Total}$ can be used to represent the area or the amplitude (or intensity) of the broad diffraction peaks in the XRD patterns of glasses and vice-versa. In this case, the ratio of S_{FSDP}/S_{Total} or the population of the structural units which produce the FSDP can be correlated to its area.

5. Conclusion

Two types of As_2S_3 glasses such as glass I and glass have been prepared respectively by slow and rapid quenching methods. The X-Ray Powder Diffraction method has been used to study these materials by recording their powder X-Ray Diffraction (XRD) patterns which show the total vitrification of the glasses. The fitting of the XRD patterns enables to have access of the characteristics of the broad peaks such as the area, the amplitude, position (2θ), and the FWHM. For the three broad peaks located at different angles 2θ between 15°-22°, 30°-38° and 50°-60°, the area, the amplitude and the position (2θ) decrease in the case of each glass.

The repetitive distance (R_1), the correlation structural length (L_1) and the ratio S_{FSDP}/S_{Total} of the FSDP have been determined. R_1 of FSDP being equal to 4.939 Å for glass I and also equal to 4.971 Å for glass II indicates that the FSDP appears at the same position in the real space because the obtained values of R_1 in the two cases are nearly the same. The parameter L_1, considered as the size of structures responsible of FSDP (or the correlation length over which the quasi-periodic real space density fluctuations are maintained) for glass I (18.480 Å) is lower than that of glass II (20.074 Å) and it is more modified by the rapid quenching method than the slow quenching method. The calculated values of S_{FSDP}/S_{Total} of glass I being higher than that of glass II indicates that rapid quenching method produces more structural units forming the FSDP. The quenching methods can modify the medium range order of the First Sharp Diffraction Peak (FSDP) characterized by the mentioned above parameters.

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