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XRD AND EDS CHARACTERIZATION OF SOME Sb_2S_3-As_2S_3-Sb_2Te_3 GLASSES PREPARED BY RAPID QUENCHING METHOD

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Some binary Sb_2S_3-As_2S_3 and ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses have been characterized by means of X-Ray powder diffraction (XRD) and Electron Dispersion Spectroscopy (EDS). The recorded diffractograms of the studied materials by the X-Ray powder diffraction (XRD) method have shown their vitreous state. The chemical composition of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses measured by EDS has indicated little observed variations of atomic percentage from 0% to 2% between the experimental and the theoretical results for the constituent atoms of binary and ternary vitreous materials of the above system prepared by rapid quenching method in ice water. In spite of these observed variations of the atomics' percentages, it has been admitted that, the preparation method of binary Sb_2S_3-As_2S_3 and ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses in sealed tubes could be satisfactory and could give reproducible results.

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Keywords: Glasses, X-ray powder diffraction (XRD), Electron Dispersion Spectroscopy (EDS).

1. Introduction

A great deal of work has been done to determine the structure of glasses using X-ray or neutron diffraction [1]. The investigation of chalcogenide glasses (S, Se and Te) has recently drawn great attention of solid-state physicists and electronic engineers because of the many actual and potential technological applications of these materials in solid-state devices [2-6].

The Sb_2S_3-As_2S_3-Sb_2Te_3 system is a prototypical chalcogenide system and forms bulk glasses by melt-quenching in a wide range of compositions in binaries systems (Sb_2S_3-As_2S_3, Sb_2S_3-As_2S_3 and Sb_2Te_3-Sb_2S_3) and ternary sections (with constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol %) in the above ternary system [7]. This system is composed of As_2S_3 the excellent glass former [7], Sb_2S_3 with poor glass-forming ability [8] and Sb_2Te_3 which does not form glass by a conventional quenching method [7]. Therefore, it provides a model system for performing studies on structural changes as a function of composition.

This work reports recent results of our studies concerning the characterization of the vitreous materials obtained in Sb_2S_3-As_2S_3-Sb_2Te_3 system by rapid quenching method in ice water.

2. Experimental

Mixtures of pure (>99.99%) elements with the nominal composition of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses were prepared by direct synthesis from pure starting elements such as As, Sb, S and Te. Quartz ampoules were filled with the mixed elements and then evacuated to ~ 10^{-3} torr, sealed

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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 rapidly in ice-water.

X-Ray powder diffraction (XRD) of the samples was recorded at room temperature using a Philips PW 1050 X-ray diffractometer with Cu-Kα radiation (λ=1.54185Å) and 2θ range from 10 to 60°, working at 40 kV and 20 mA. The scanning in 2θ steps is 0.04° and the integration time is 17.5s/point.

Analysis using Energy-dispersive X-ray spectroscopy (EDS) permits to control the real stoichiometry of the studied glasses by comparing the experimental results with the theoretical ones concerning the chemical composition.

3. Results

3. 1 Analysis of X-ray diffractograms of binary and ternary glasses

Figure 1 shows the diffractograms of some binary compositions of the Sb_2S_3-As_2S_3 system with As_2S_3 content varying from 10 to 100 mol%. For the compositions having As_2S_3 contents equal to 10 mol %, 25 mol % and 50 mol %, four halo diffusion peaks are observed with 2θ located between 15°-20°, 20°-30°, 30°-40° and 45°-60°. Whereas three halo diffusion peaks, for 2θ values between 15°-20°, 25°-35° and 50°-60°, are observed for Sb_2S_3-As_2S_3 compositions with 75 and100 mol% of As_2S_3.

The intensity of the first halo diffusion peak, located between 15° and 20° on XRD of glasses, increases with the increasing of the content of As_2S_3. For glasses with As_2S_3 content varying from 10 mol % to 50 mol % (figure 1) the intensity of the located second halo diffusion peak at 2θ between 20° and 30° decreases. Above 50 mol% of As_2S_3, this second diffusion halo peak disappears

The intensities of the first and the second diffusion halo peaks are compared with those of the most intensive peaks of crystallized As_2S_3 [9] (figure 1) and Sb_2S_3 [10] (figure 2) in order to verify the assertion made by Popescu [11]

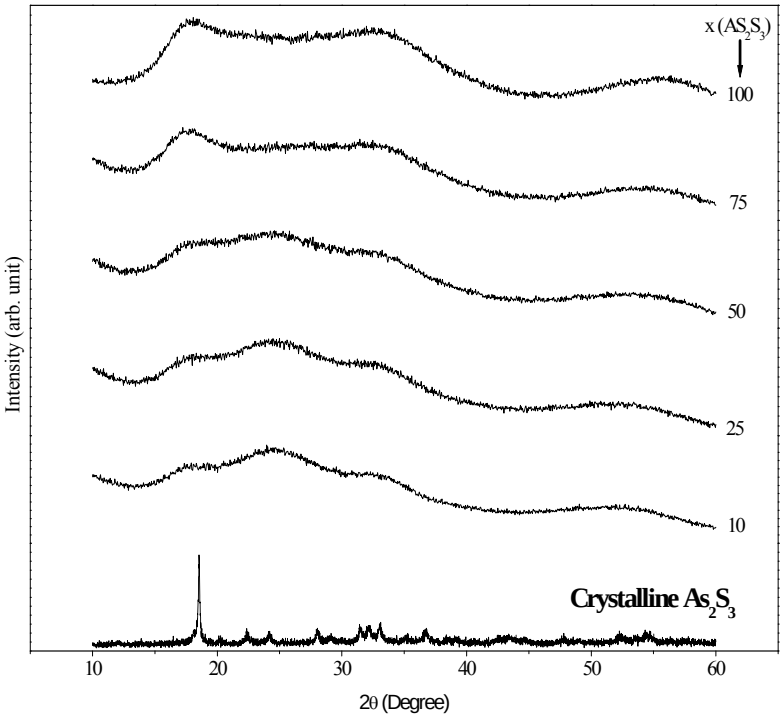


Figure 1 : Comparison of X-Ray diffraction patterns of Sb_2S_3-As_2S_3 glasses with the diffractogram of crystallized As_2S_3

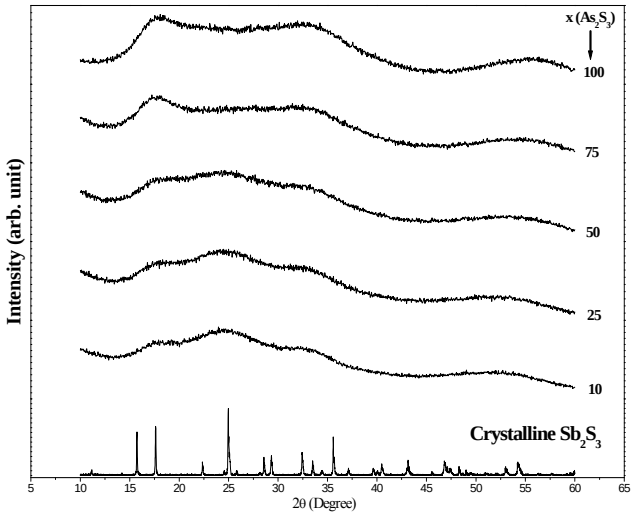


Figure 2 : Comparison of X-Ray diffraction patterns of glasses of the Sb_2S_3-As_2S_3 system with the diffractogram of crystalline Sb_2S_3

From figure 1 or 2, it can be suggested that the presence of As_2S_3 in greater quantity diminishes the number of the halo diffusion peaks from four (for As_2S_3 mol % between 10 and 50) to three when the content of As_2S_3 is beyond 50 mol%. In this case, the diffusion halo peak located at 2θ values between 20° and 30° does not appear.

Figures 3, 4 and 5 represent the evolution of XRD patterns of ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses (containing constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol %) as a function of As_2S_3 content. The X-Ray patterns of ternary glasses at constant Sb_2Te_3 concentrations of 10 mol % (figure 4) and 20 mol % (figure 5) are characterized by four halo diffusion peaks for As_2S_3 content between 10 and 50 mol%.

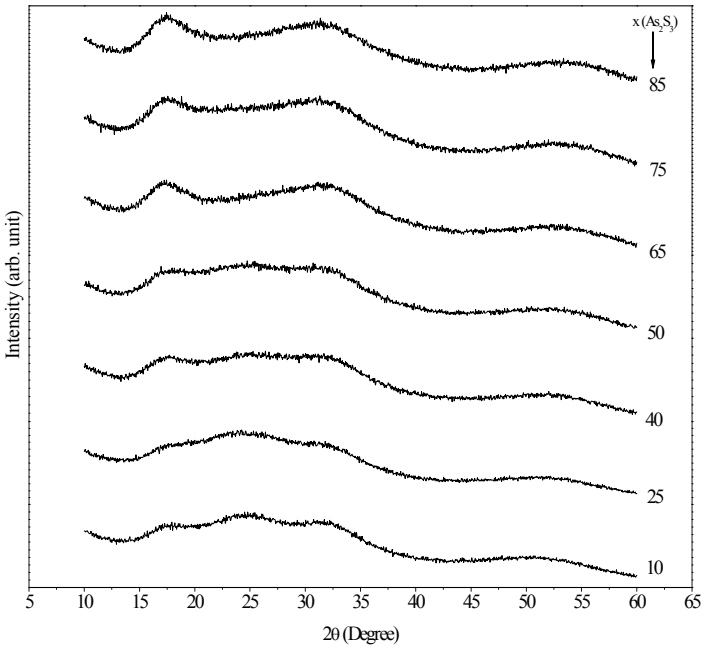


Figure 3 : X-Ray diffraction patterns of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses at constant Sb_2Te_3 concentration of 10 mol %

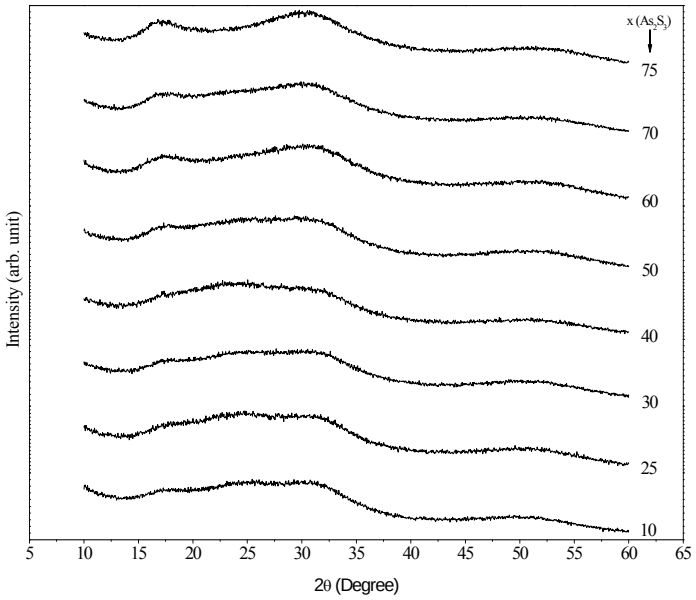


Figure 4 : X-Ray diffraction patterns of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses at constant Sb_2Te_3 concentration of 20 mol %

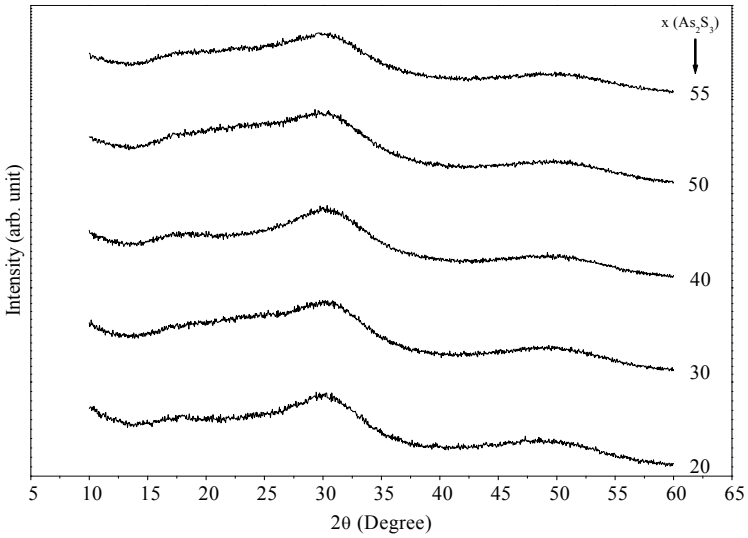
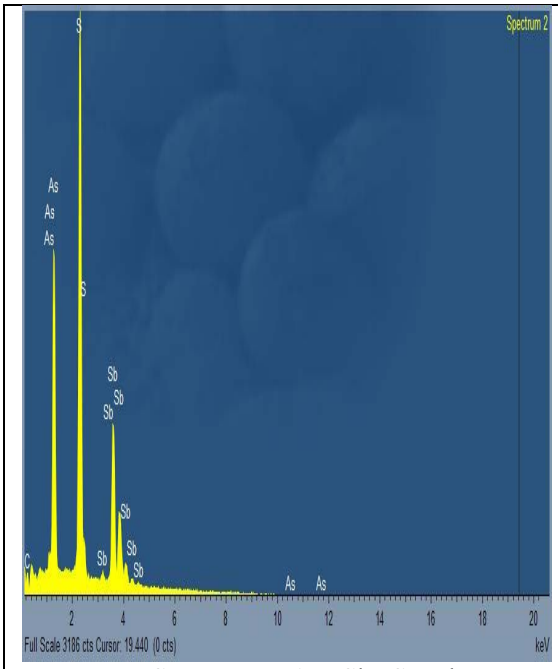


Figure 5 : X-Ray Diffraction patterns of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses at constant Sb_2Te_3 concentration of 40 mol %

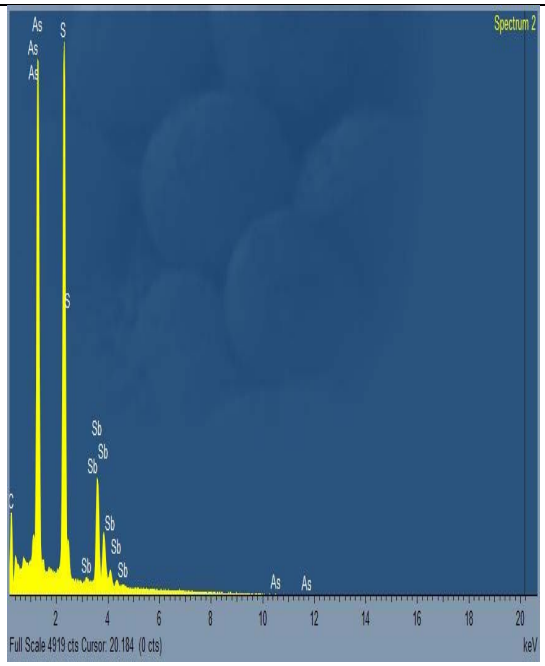
But for As_2S_3 content beyond 50 mol%, the XRD of these glasses (figures 3 and 4) and those of glasses containing 40% Sb_2Te_3 (figure 5) present three halo diffusion peaks. It can be noted that the halo diffusion peak appearing at 2θ between 20°-30° is not observed on the XRD patterns for ternary glasses with constant mol % Sb_2Te_3 equal to 40.

3. 2 Analysis of the chemical composition of binary and ternary glasses by EDS

The chemical composition of various vitreous powder samples of the Sb_2S_3-As_2S_3-Sb_2Te_3 system corresponds to the average of three analyses. The aim of these analyses is to verify if the samples preparation method in sealed tubes is satisfactory and gives reproducible results. Thus the experimental atomic percentages are compared with the theoretical values of atomic percentages. Figure 7 below indicates EDS spectra of two Sb_2S_3-As_2S_3 glasses taken as examples.



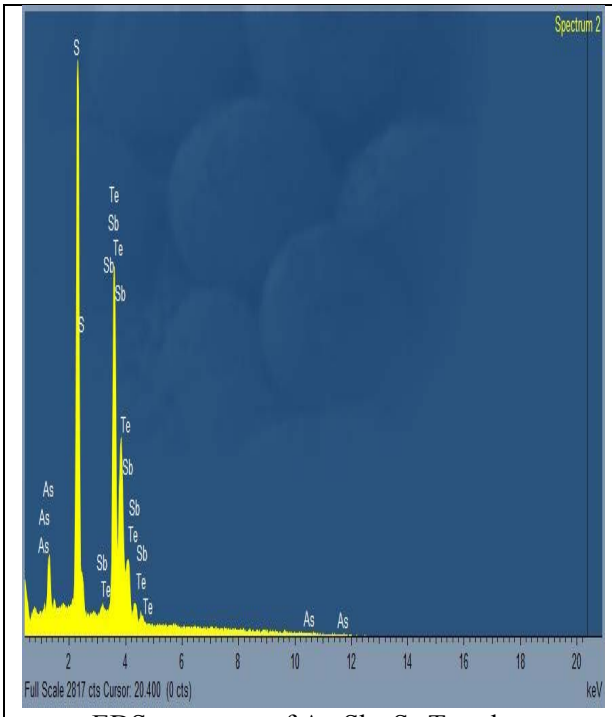
EDS spectrum $As_{26}Sb_{14}S_{60}$ glass



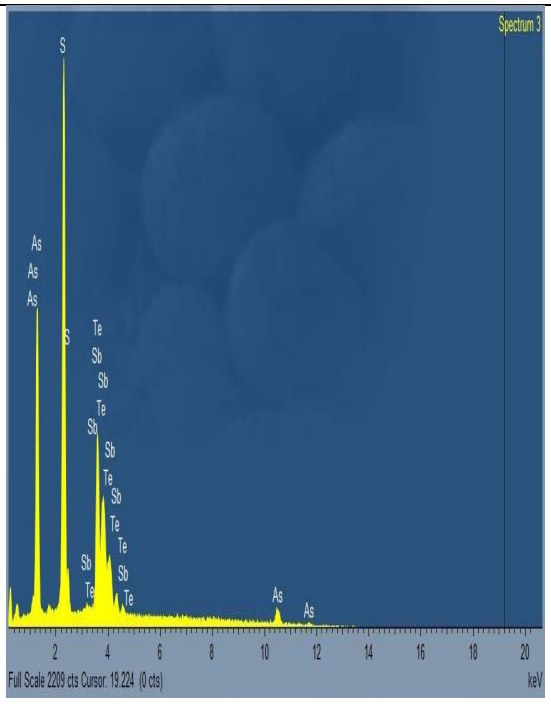
EDS spectrum $As_{30}Sb_{10}S_{60}$ glass

Fig. 7 : EDS Spectra of two vitreous composition of Sb_2S_3-As_2S_3 system

EDS spectra of ternary glasses containing 10, 20 and 40 mol % of Sb_2Te_3 are represented respectively by figures 8, 9 and 10. Figures 7 to 10 indicate that the intensity of the peak corresponding to the sulfur atom in binary and ternary glasses remains practically unchanged in each case. But the intensities of the peaks concerning arsenic (or antimony) atom increase (or decrease) when its content increases (or decreases) for binary and ternary glasses. It should be noted that the peaks corresponding to antimony (Sb) and tellurium (Te) atoms overlap and are not distinct like those of sulfur or arsenic.

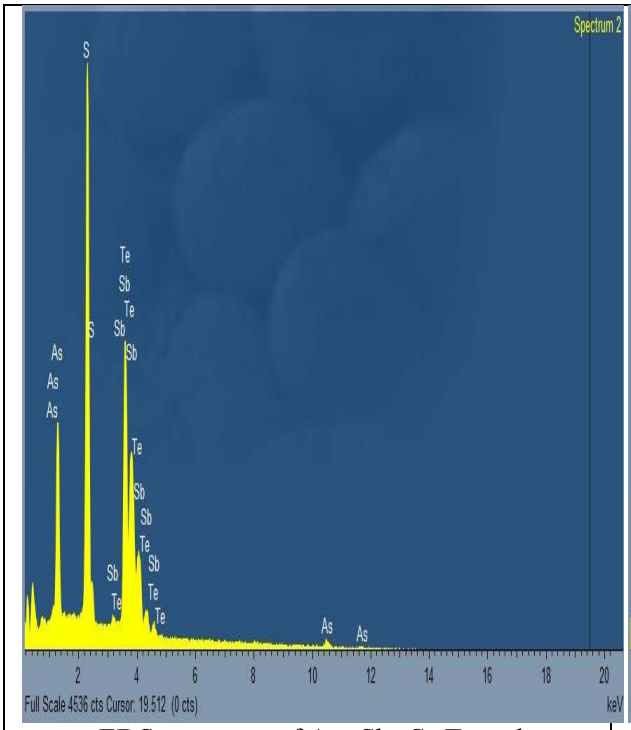


EDS spectrum of $As_4Sb_{36}S_{54}Te_6$ glass

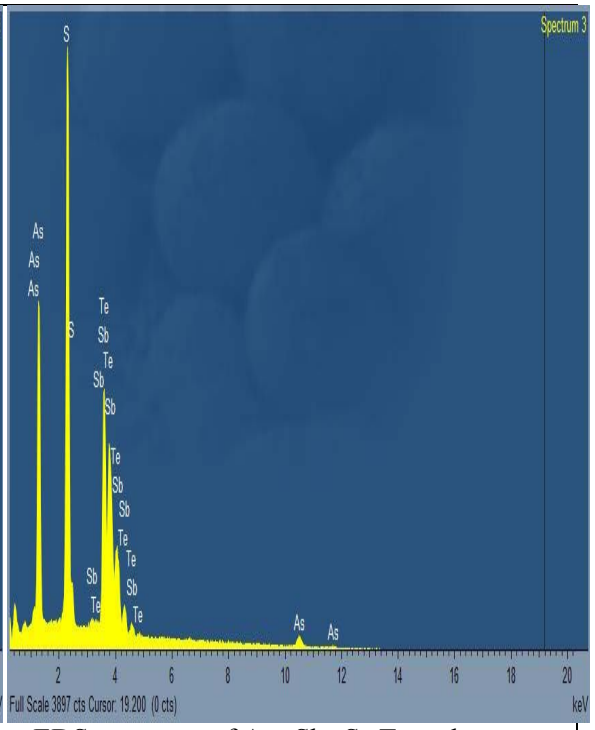


EDS spectrum of $As_{26}Sb_{14}S_{54}Te_6$ glass

Fig. 8 : EDS Spectra of two vitreous compositions in Sb_2S_3-As_2S_3-Sb_2Te_3 system at constant 10 mol% of Sb_2Te_3

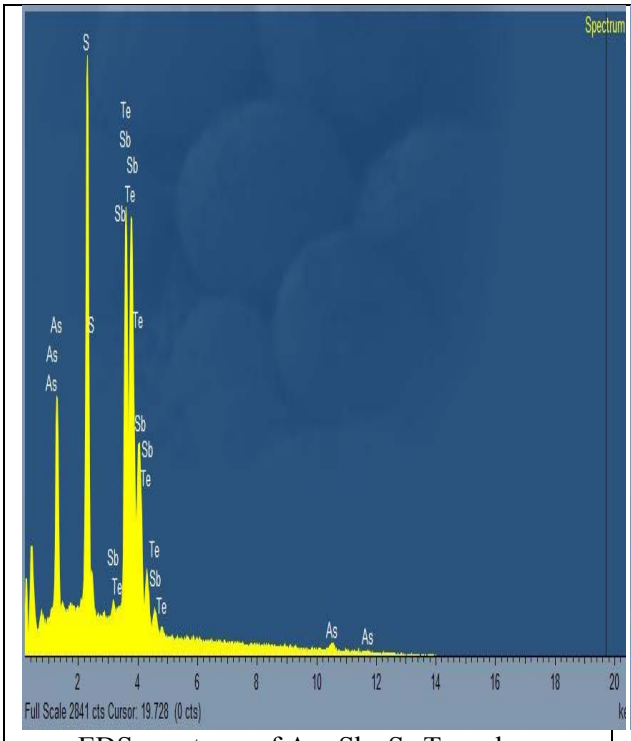


EDS spectrum of $As_{12}Sb_{28}S_{48}Te_{12}$ glass

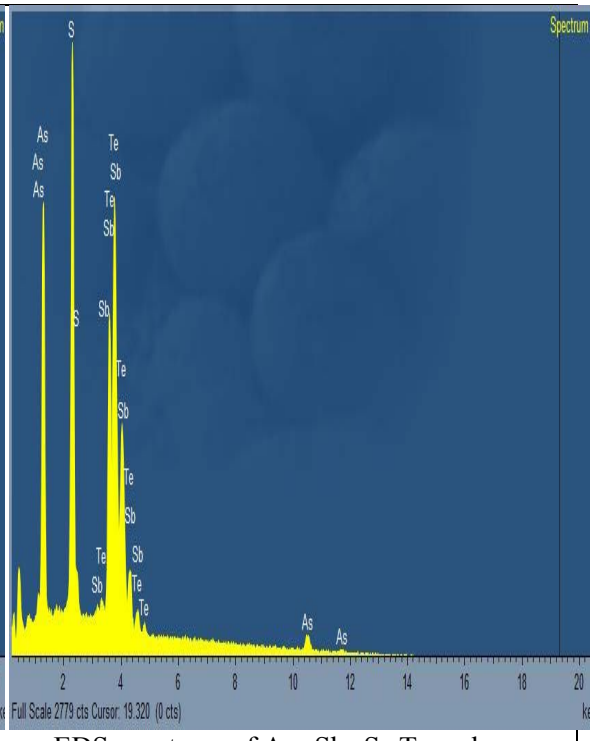


EDS spectrum of $As_{20}Sb_{20}S_{48}Te_{12}$ glass

Fig. 9 : EDS Spectra of two vitreous compositions in Sb_2S_3-As_2S_3-Sb_2Te_3 system at constant 20 mol% of Sb_2Te_3



EDS spectrum of $As_{12}Sb_{28}S_{36}Te_{24}$ glass



EDS spectrum of $As_{22}Sb_{18}S_{36}Te_{24}$ glass

Fig. 10 : EDS Spectra of two vitreous compositions in Sb_2S_3-As_2S_3-Sb_2Te_3 system at constant 40 mol% of Sb_2Te_3

Tables 1, 2, 3 and 4 below indicate the results from EDS analyses for some binary and ternary glasses of Sb_2S_3-As_2S_3-Sb_2Te_3 system.

Table 1: EDS chemical analysis of Sb_2S_3-As_2S_3 glasses.

Samples	Theoretical atomic %	Experimental atomic %	β_1	β_2
$As_{40}S_{60}$	40 / 00 / 60	41.42 / 58.58	0.667	0.707
$As_{30}Sb_{10}S_{60}$	30 / 10 / 60	29.64 / 10.81 / 60	0.667	0.679
$As_{20}Sb_{20}S_{60}$	20 / 20 / 60	18.97 / 21.99 / 59.04	0.667	0.694
$As_{10}Sb_{30}S_{60}$	10 / 30 / 60	10.41 / 29.19 / 60.40	0.667	0.659
$As_{04}Sb_{36}S_{60}$	04 / 36 / 60	03.74 / 36.47 / 59.79	0.667	0.673

Table 2: EDS chemical analysis of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing 10 mol % of Sb_2Te_3

Samples	Theoretical atomic %	Experimental atomic %	β_1	β_2
$As_{34}Sb_{06}S_{54}Te_{06}$	34 / 06 / 54 / 06	33.13 / 06.49 / 54.16 / 06.21	0.667	0.656
$As_{30}Sb_{10}S_{54}Te_{06}$	30 / 10 / 54 / 06	30.02 / 09.97 / 54.24 / 05.77	0.667	0.666
$As_{16}Sb_{24}S_{54}Te_{06}$	16 / 24 / 54 / 06	14.84 / 25.83 / 52.45 / 06.89	0.667	0.685
$As_{04}Sb_{36}S_{54}Te_{06}$	04 / 36 / 54 / 06	04.08 / 36.48 / 52.74 / 06.70	0.667	0.682

Table 3: EDS chemical analysis of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing 20 mol % of Sb_2Te_3

Samples	Theoretical atomic %	Experimental atomic %	β_1	β_2
$As_{28}Sb_{12}S_{48}Te_{12}$	28 / 12 / 48 / 12	26.36 / 12.69 / 46.30 / 14.65	0.667	0.641
$As_{20}Sb_{20}S_{48}Te_{12}$	20 / 20 / 48 / 12	18.48 / 21.39 / 47.63 / 12.50	0.667	0.663
$As_{12}Sb_{28}S_{48}Te_{12}$	12 / 28 / 48 / 12	11.24 / 29.76 / 46.34 / 12.66	0.667	0.694
$As_{10}Sb_{30}S_{48}Te_{12}$	10 / 30 / 48 / 12	09.91 / 30.18 / 47.79 / 12.12	0.667	0.669
$As_{04}Sb_{36}S_{48}Te_{12}$	04 / 36 / 48 / 12	03.72 / 37.93 / 46.05 / 12.30	0.667	0.714

Table 4: EDS chemical analysis of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing 40 mol % of Sb_2Te_3

Samples	Theoretical atomic %	Experimental atomic %	β_1	β_2
$As_{16}Sb_{24}S_{36}Te_{24}$	16 / 24 / 36 / 24	14.35 / 25.97 / 34.50 / 25.18	0.667	0.676
$As_{12}Sb_{28}S_{36}Te_{24}$	12 / 28 / 36 / 24	11.25 / 28.93 / 35.41 / 24.41	0.667	0.672

β_1 = Theoretical ratio (As+Sb)/(S+Te) and β_2 = Experimental ratio (As+Sb)/(S+Te).

The above tables indicate that the sum of the determined atomic percentages (obtained experimentally) of the different elements constituting each glass is equal to 100%. Moreover the comparison between the theoretical ratio (β_1) and experimental one (β_2) gives similar values. But it should be noted that little variations from 0% to 2% are observed between the experimental and the theoretical results for the constituent atoms belonging to Sb_2S_3-As_2S_3-Sb_2Te_3 system.

4. Discussions

The presence of the halo diffusion peaks observed on the XRD patterns of binary Sb_2S_3-As_2S_3 and ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses indicates that their obtained diffractograms are characteristic of non-crystalline materials (figures 1 to 5).

Among the compounds constituting Sb_2S_3-As_2S_3-Sb_2Te_3 system, As_2S_3 is the excellent glass former [7], Sb_2S_3 has a poor glass-forming ability [8] and Sb_2Te_3 does not form glass by a conventional quenching method [7]. So the increasing of the intensity of the first diffraction peak for 2θ between 15° and 20° when the content of As_2S_3 increases can be related to the glass-forming ability of the formed glasses. In this case, the glass-forming ability of the vitreous

materials increases with the increase in As_2S_3 content in each section of Sb_2S_3-As_2S_3-Sb_2Te_3 system. Thus, on binary Sb_2S_3-As_2S_3 system and ternary Sb_2S_3-As_2S_3-Sb_2Te_3 system (with constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol %), the intensity of the first diffraction peak is favored by the increase in As_2S_3 content. The opposed behavior is observed for the increasing of Sb_2S_3 content. The decreasing of the intensity of the first diffraction peak with the increasing of Sb_2S_3 content can be also related to the glass-forming ability of the obtained glasses. So the glass-forming ability of the glasses diminishes when the concentration of Sb_2S_3. For the binary Sb_2S_3-As_2S_3 and ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses, the intensity of the first diffraction peak can be used to estimate the glass-forming ability among the obtained materials when the content of As_2S_3 increases.

The first halo diffusion peak appearing between 15° and 20° can be attributed to the vitreous form of As_2S_3 compound because this halo diffusion peak corresponds approximately to the one of the most intensive peaks of the aforesaid compound in its crystallized form (figure 1). The second halo diffraction peak located at 2θ between 20° and 30° can be attributed to that of Sb_2S_3 glass because this diffusion peak corresponds approximately to one of the most intensive peaks of crystalline Sb_2S_3 (figure 2). The above two assertions are in agreement with M. A. Popescu [11] who observes that in many chalcogenide glasses the broad maxima are located at the positions where intense diffraction peaks exist in the crystalline homologs.

Beyond 50 mol % of As_2S_3 in Sb_2S_3-As_2S_3 system (figures 1 and 2) and in ternary Sb_2S_3-As_2S_3-Sb_2Te_3 system with constant concentration of Sb_2Te_3 at 10 and 20 mol% (figures 3 and 4), the halo diffraction peak belonging to the vitreous phase of Sb_2S_3 and appearing for 2θ values between 20° and 30° is not observed. That is also valid for the XRD patterns of ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses containing 40 mol% of Sb_2Te_3 (figure 5). The vitreous matrix is homogeneous where Sb_2S_3 could be dispersed. From the above observations, we can suggest that Sb_2S_3-As_2S_3 glasses are composed of mixture of vitreous phases of As_2S_3 and Sb_2S_3. These materials are formed by the structural units of As_2S_3 and Sb_2S_3. But for Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol%, their structure can be suggested to be composed of structural units of Sb_2S_3, As_2S_3 and Sb_2Te_3. For As_2S_3 content above or below 50 mol%, the glasses could have the same basic structure because their diffractograms seem to be similar.

The unchanged intensity of sulfur atoms on EDS spectra in each case of binary and ternary of Sb_2S_3-As_2S_3-Sb_2Te_3 system can be related to the constant percentages of this atom which are equal to 60% (Sb_2S_3-As_2S_3 system), 54% (10 mol% of Sb_2Te_3), 48% (20 mol% of Sb_2Te_3) and 36% (40 mol% of Sb_2Te_3).

The observed overlap of the peaks corresponding to antimony and tellurium atoms on EDS spectra for ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol% can be probably explained by the similar physical characteristics these two atoms. Indeed, antimony (Sb) and tellurium (Te) have atomic masses equal to 121.8g/mol and 127.6g/mol respectively. Their respective atomic numbers are equal to 51 and 52.

The sum of the determined atomic percentages (obtained experimentally) of the different elements constituting each glass (tables 1-4) being equal to 100% indicates that, no lost of constituent elements during the synthesis of these materials appears. But the variations from 0% to 2% are observed between the experimental and the theoretical results for the constituent atoms belonging to Sb_2S_3-As_2S_3-Sb_2Te_3 system can be probably explained by the fact that the refining which consists in agitating the molten mixture was not well adjusted to obtain homogeneous compositions with the theoretical composition.

In spite of these observed variations concerning the measured experimental percentages of the atoms, the samples of the binary Sb_2S_3-As_2S_3 system and those of ternary Sb_2S_3-As_2S_3-Sb_2Te_3 system (three sections of samples with the constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol%) have experimental compositions close to the theoretical ones. In this case, the preparation method of samples in sealed tubes is satisfactory and gives reproducible results.

5. Conclusions

Two characterization techniques such as X-Ray powder diffraction (XRD) method and Electron Dispersion Spectroscopy (EDS) have been used to study binary and ternary glasses in Sb_2S_3-As_2S_3-Sb_2Te_3 system.

The X-Ray powder Diffraction method has indicated that the binary Sb_2S_3-As_2S_3 glasses are composed of structural units deriving from Sb_2S_3 and As_2S_3 compounds. But the ternary Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol% are made up structural units of Sb_2S_3, As_2S_3 and Sb_2Te_3.

Analysis obtained by EDS has shown that the preparation method of samples in sealed tubes is satisfactory and gives reproducible results.

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