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Study of some numerical characteristic parameters of Sb_2S_3-As_2S_3-Sb_2Te_3 vitreous compositions calculated from their chemical formula obtained by EDS experiments

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Glasses of binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3) belonging to Sb_2S_3-As_2S_3-Sb_2Te_3 system were prepared by rapid quenching method in ice water of their liquid phases. From chemical formulas obtained by using Energy Dispersion Spectroscopy (EDS), average values of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses' parameters such as coordination number (Z), atomic radius (R_{av}), atomic number (Z_{av}), atomic molar mass (M_{av}) and electronegativity (χ_{av}) were calculated. These parameters were used to explain the formation of the glasses in the Sb_2S_3-As_2S_3-Sb_2Te_3 system by following their evolution as a function of the As_2S_3 content.

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1. Introduction

The Sb_2S_3-As_2S_3-Sb_2Te_3 system is a chalcogenide prototype which forms glasses in a wide range of compositions in binary systems (Sb_2S_3-As_2S_3, Sb_2Te_3-As_2S_3 and Sb_2Te_3-Sb_2S_3) and ternary sections containing 10 mol%, 20 mol% and 40 mol% of Sb_2Te_3 [1].

In addition of the experimental conditions (quantity of material, cooling rate or quenching rate, quenching medium, quenching temperature and pressure) enabling the formation of non-crystalline materials, there are own specific parameters of liquids which participate to their vitrification during cooling.

These intrinsic parameters are the average values of the coordination number, the atomic radius, the atomic number, the atomic molar mass and the electronegativity of the atoms constituting the liquids (or the compositions) used to form glassy materials.

The aim of this article is to theoretically calculate, from the chemical formulas obtained by EDS, the mean values of the intrinsic parameters (mentioned above) of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses which can be used to explain the glass formation region in the studied system. This can be done by following the evolutions of these intrinsic parameters on binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (with constant concentrations of Sb_2Te_3 at 10, 20 and 40 mol %) as a function of As_2S_3 content.

Indeed, the previous studies have shown that among the compounds of Sb_2S_3-As_2S_3-Sb_2Te_3 system, As_2S_3 is an excellent glass former (by forming glass alone), Sb_2S_3 and Sb_2Te_3 do not form glasses by a conventional quenching method [1]. According to [2], Sb_2S_3 has a poor glass-forming ability and it can form glass alone at high cooling rate. Therefore, glass forming ability of As_2S_3 is higher than that of Sb_2S_3 and Sb_2Te_3.

Theoretical calculations carried out from the experimental formulas obtained by energy dispersion spectroscopy (EDS) can enable us to know the intervals of the intrinsic parameters' values that can be fulfilled by Sb_2S_3-As_2S_3-Sb_2Te_3 compositions to form glasses on binary systems

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(Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10%, 20% and 40% of Sb_2Te_3) during the rapid cooling of the liquids phases of the materials.

2. Experimental

Glasses of Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3 systems, 10 mol% Sb_2Te_3, 20 mol% Sb_2Te_3 and 40 mol% Sb_2Te_3 sections in Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system, having respective formulas $As_{0.4x}Sb_{0.4(100-x)}S_{60}$ (x=10, 25, 50, 50, 100), $As_{0.4x}Sb_{0.4(100-x)}S_{0.6x}Te_{0.6(100-x)}$ (x=40, 50, 60, 70, 80, 90, 100), $As_{0.4x}Sb_{0.4(100-x)}S_{54}Te_{06}$ (x=10, 30, 45, 60), $As_{0.4x}Sb_{0.4(100-x)}S_{48}Te_{12}$ (x=10, 30, 45, 60) and $As_{0.4x}Sb_{0.4(100-x)}S_{36}Te_{24}$ (x=10, 25, 40) where x is As_2S_3 mol%, are prepared by direct synthesis from pure starting elements such as As (99.999%), Sb (99.999%), S (99.999%) and Te (99.998%). Quartz ampoules were filled with 300±0.1 mg of 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 rapidly in ice-water.

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 glassy state in the quenched samples is confirmed as no sharp peak is observed on their XRD patterns.

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. Nature of samples by X-Ray powder diffraction (XRD) method

Samples of Sb_2S_3-As_2S_3 (with 10, 25, 50, 75 and 100 mol% of As_2S_3) and Sb_2Te_3-As_2S_3 (with 40, 50, 60, 70, 80, 90 and 100 mol% of As_2S_3) systems, those of 10 mol% (with 30, 60 and 80 mol% of As_2S_3), of 20 mol% (with 10, 25, 30, 50, 70 mol% of As_2S_3) and of 40 mol% (with 25, 40 and 60 mol% of As_2S_3) Sb_2Te_3 sections in Sb_2S_3-As_2S_3-Sb_2Te_3 system have been investigated.

X-Ray diffraction patterns (taken as examples) of the studied samples in the Sb_2S_3-As_2S_3-Sb_2Te_3 system are shown in figure 1. Broad diffraction peaks are observed in all of the diffraction patterns of these materials in the range of diffraction angles 2θ from 10 to 60° (θ is the Bragg angle).

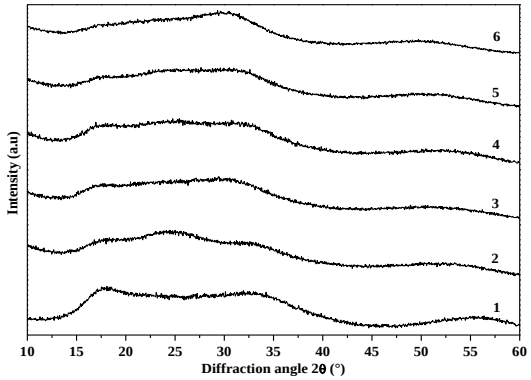

Fig. 1. X-Ray diffraction patterns (taken as examples) of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with their chemical composition in mol% of As_2S_3, Sb_2S_3 and Sb_2Te_3 : 1. 100% As_2S_3, 2. 25% As_2S_3-75%Sb_2S_3, 3. 80%As_2S_3-20%Sb_2Te_3, 4. 50%As_2S_3-40%Sb_2S_3-10%Sb_2Te_3, 5. 30%As_2S_3-50%Sb_2S_3-20%Sb_2Te_3 and 6. 50%As_2S_3-10%Sb_2S_3-40%Sb_2Te_3).

3.2. Comments on the chemical composition of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses.

The chemical composition of various powder samples of Sb_2S_3-As_2S_3-Sb_2Te_3 system corresponds to the average of three analyses. The results of EDS analyses for some binary and ternary samples of Sb_2S_3-As_2S_3-Sb_2Te_3 system are presented in tables 1-5 [3].

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

As_2S_3 mol%	Theoretical atomic %			Experimental atomic %		
	As	Sb	S	As	Sb	S
10	04	36	60	**03.74**	36.47	**59.79**
25	10	30	60	10.41	**29.19**	60.40
50	20	20	60	**18.97**	21.99	**59.04**
75	30	10	60	**29.64**	10.81	60.00
100	40	00	60	41.42	00.00	**58.58**

Table 2. EDS chemical analysis of Sb_2Te_3-As_2S_3 glasses.

As_2S_3 mol%	Theoretical atomic %				Experimental atomic %			
	As	Sb	S	Te	As	Sb	S	Te
50	20	20	30	30	**18.22**	22.09	**25.74**	33.95
60	24	16	36	24	**23.28**	**15.79**	36.66	24.28
70	28	12	42	18	**27.87**	**11.59**	42.43	18.10
80	32	08	48	12	**29.81**	08.45	48.70	13.04
90	36	04	54	06	**35.68**	04.14	54.23	**05.95**
100	40	00	60	00	41.42	00.00	**58.58**	00.00

Table 3. EDS chemical analysis of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with constant 10 mol% of Sb_2Te_3.

As_2S_3 mol%	Theoretical atomic %				Experimental atomic %			
	As	Sb	S	Te	As	Sb	S	Te
10	04	36	54	06	04.08	36.48	**52.74**	06.70
40	16	24	54	06	**14.84**	25.83	**52.45**	06.89
65	26	14	54	06	**22.58**	16.94	**52.91**	07.57
75	30	10	54	06	30.02	**09.97**	54.24	**05.77**
85	34	06	54	06	**33.13**	06.49	54.16	06.21

Table 4. EDS chemical analysis of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with constant 20 mol% of Sb_2Te_3.

As_2S_3 mol%	Theoretical atomic %				Experimental atomic %			
	As	Sb	S	Te	As	Sb	S	Te
10	04	36	48	12	**03.72**	37.93	**46.05**	12.30
25	10	30	48	12	**09.91**	30.18	**47.79**	12.12
30	12	28	48	12	**11.24**	29.76	**46.34**	12.66
50	20	20	48	12	**18.48**	21.39	**47.63**	12.50
70	28	12	48	12	**26.36**	12.69	**46.30**	14.65

Table 5. EDS chemical analysis of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses with constant 40 mol% of Sb_2Te_3.

As_2S_3 mol%	Theoretical atomic %				Experimental atomic %			
	As	Sb	S	Te	As	Sb	S	Te
30	12	28	36	24	**11.25**	28.93	**35.41**	24.41
40	16	24	36	24	**14.35**	25.97	**34.50**	25.18
55	22	18	36	24	**18.61**	20.40	**34.20**	26.72
60	24	16	36	24	**23.28**	**15.79**	36.66	24.28

The above tables indicate that there are slight discrepancies between the experimental and theoretical atomic percentages of the studied samples. The experimental atomic percentages in bold show slight deficiencies in arsenic (As), antimony (Sb), sulfur (S) and tellurium (Te). Those not in bold show slight excesses in the above mentionned atoms. The sum of the atomic percentages, determined experimentally, of the different elements constituting each glass is equal to 100%. In this case, there was no loss of products during the synthesis of these materials.

3.3. Parameters of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses calculated with EDS results

In this section, we give the definitions of the atomic characteristics (coordination number, atomic radius, electronegativity, atomic number and atomic molar mass) as well as the formulas of their average values when the atoms enter in the composition of the glassy materials of the system Sb_2S_3-As_2S_3-Sb_2Te_3 obtained by rapid cooling in ice water of their liquid phases.

The coordination number or coordination index or coordination of an atom in a material is the number of nearest neighbor atoms, molecules or ions in the three directions of space and connected to this atom.

The average coordination number (Z) of a material, proposed by Phillips [4,5], is the average of the coordination numbers of its constituents and predicts the connectivity of the material structure. For a composition with n constituents, the average coordination number is defined by the following expression:

$$Z = \sum_{i=1}^{n} x_i \lambda_i \quad (1)$$

where x_i is the atomic fraction of atom i. λ_i, the coordination number of atom i, is obtained by the 8-N relationship (octet rule) where N is the number of valence electrons.

The atomic radius of a chemical element is a measure of the size of its atoms, usually the average distance between the nucleus and the boundary of the electron cloud that surrounds it. As this boundary is not a well-defined physical entity, there are several non-equivalent definitions of the atomic radius. Depending on the definition, the term can apply only to single atoms, or also to atoms in condensed matter, a covalent bond in a molecule or in ionized and excited states. Its value can be obtained by experimental measurements or calculated from theoretical models. With certain definitions, the value of the atomic radius can depend on the atomic state and its environment [6]. Atoms can often be modeled as spheres. This approximation can provide explanations and predictions for many phenomena such as the density of fluids and solids, the diffusion of fluids in a molecular sieve, the arrangement of atoms and ions in crystals and the size and shape of molecules. The average atomic radius (R_{av}) of a material is the average of the atomic radii of the constituents that make up this material. Its expression is the following:

$$R_{av} = \sum_{i=1}^{n} x_i R_i \quad (2)$$

where x_i and R_i are the fraction and radius of atom i respectively.

The atomic number is the number of electrons that an atom has on its electronic structure. The arrangement of all the electrons around the nucleus constitutes the electronic cloud of the atom. The greater the distance between the outer electrons and the nucleus (high atomic number), the less these electrons will be under the influence of the nucleus and they will be extracted easily.

The smaller the distance (low atomic number), the more these electrons will be under the influence of the nucleus and it will take a lot of energy to extract them. The average atomic number (Z_{av}) of a material is the average of the atomic numbers of the constituent atoms of the material. It can be defined by the following expression:

$$Z_{av} = \sum_{i=1}^{n} x_i Z_i \quad (3)$$

where x_i and Z_i are respectively the fraction and the atomic number of the atom i.

The atomic molar mass of an element is the mass of one mole of atom of this element. The average atomic molar mass (M_{av}) of a material is the average of the atomic molar masses of the atoms making up the material. It can be defined by the following expression:

$$M_{av} = \sum_{i=1}^{n} x_i M_i \quad (4)$$

where x_i is an integer or not in its irreducible form (in the formula of the composition) and M_i is the molar mass of atom i.

Electronegativity is defined as the ability of an atom to attract electrons when it is in bond with another atom or it is the tendency of an element to attract to it the electrons of the bond. The average electronegativity (χ_{av}) of a material is the average of the electronegativities of its constituent atoms. Its expression is the following:

$$\chi_{av} = \sum_{i=1}^{n} x_i \chi_i \quad (5)$$

where x_i and χ_i are the fraction and electronegativity of atom i respectively.

From the characteristics of antimony (Sb), arsenic (As), sulfur (S) and tellurium (Te) atoms (Table 6), it was possible to calculate the average coordination number (Z), the average electronegativity (χ_{av}), the average atomic radius (R_{av}), the average atomic number (Z_{av}) and the average atomic molar mass (M_{av}) of binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3) glasses belonging to Sb_2S_3-As_2S_3-Sb_2Te_3 system. The average values of the above characteristics are grouped in Tables 6-11.

Table 6. Coordination number (λ_i), atomic radius (R_i), atomic number (Z_i), atomic molar mass (M_i) and electronegativity (χ_i) for each constitutive element of Sb_2S_3-As_2S_3-Sb_2Te_3 system.

Atom	λ_i	R_i (Å) [9]	Z_i [2]	M_i (g.mol^{-1}) [9]	χ_i [9]
Sb	3	1.45	51	121.760	2.05
As	3	1.15	33	074.922	2.18
S	2	1.00	16	032.065	2.58
Te	2	1.40	52	127.600	2.10

Table 7. Average values of coordination number (Z), atomic radius (R_{av}), atomic number (Z_{av}), atomic molar mass (M_{av}) and electronegativity (χ_{av}) for Sb_2S_3-As_2S_3 glasses.

As_2S_3 mol%	Z	R_{av} (Å)	Z_{av}	M_{av} (g.mol^{-1})	χ_{av}
10	2.402	1.170	29.400	330.347	2.372
25	2.396	1.147	27.986	316.296	2.384
50	2.409	1.127	26.921	292.877	2.387
75	2.404	1.093	24.822	269.458	2.404
100	2.414	1.062	23.041	246.039	2.414

Table 8. Average values of coordination number (Z), atomic radius (R_{av}), atomic number (Z_{av}), atomic molar mass (M_{av}) and electronegativity (χ_{av}) for Sb_2Te_3-As_2S_3 glasses.

As_2S_3 mol%	Z	R_{av} (Å)	Z_{av}	M_{av} (g.mol^{-1})	χ_{av}
50	2.403	1.263	39.051	436.179	2.227
60	2.391	1.203	34.226	398.151	2.287
70	2.394	1.166	31.309	360.123	2.320
80	2.383	1.135	28.720	322.095	2.353
90	2.398	1.096	25.657	284.067	2.387
100	2.414	1.062	23.041	246.039	2.414

Table 9. Average values of coordination number (Z), atomic radius (R_{av}), atomic number (Z_{av}), atomic molar mass (M_{av}) and electronegativity (χ_{av}) for 10 mol% Sb_2Te_3 section glasses in Sb_2S_3–As_2S_3–Sb_2Te_3 system.

As_2S_3 mol%	Z	R_{av} (Å)	Z_{av}	M_{av} (g.mol^{-1})	χ_{av}
10	2.406	1.197	31.874	359.008	2.338
40	2.407	1.166	30.045	330.905	2.351
65	2.395	1.140	28.493	307.486	2.363
75	2.400	1.113	26.670	298.118	2.379
85	2.396	1.104	26.138	288.751	2.383

Table 10. Average values of coordination number (Z), atomic radius (R_{av}), atomic number (Z_{av}), atomic molar mass (M_{av}) and electronegativity (χ_{av}) for 20 mol% Sb_2Te_3 section glasses in Sb_2S_3–As_2S_3–Sb_2Te_3 system.

As_2S_3 mol%	Z	R_{av} (Å)	χ_{av}	M_{av} (g.mol^{-1})	Z_{av}
10	2.416	1.225	2.305	387.668	34.336
25	2.401	1.199	2.322	373.617	32.611
30	2.410	1.201	2.316	368.933	32.884
50	2.399	1.174	2.333	350.198	31.128
70	2.390	1.155	2.337	331.463	30.197

Table 11. Average values of coordination number (Z), atomic radius (R_{av}), atomic number (Z_{av}), atomic molar mass (M_{av}) and electronegativity (χ_{av}) for 40 mol% Sb_2Te_3 section glasses in Sb_2S_3–As_2S_3–Sb_2Te_3 system.

As_2S_3 mol%	Z	R_{av} (Å)	Z_{av}	M_{av} (g.mol^{-1})	χ_{av}
30	2.402	1.245	36.826	426.254	2.264
40	2.403	1.239	36.594	416.887	2.264
55	2.391	1.227	35.947	402.835	2.269
60	2.391	1.203	34.226	398.151	2.287

Tables 7-11 indicate that glasses are formed in the Sb_2S_3-As_2S_3-Sb_2Te_3 system for values of average coordination number between 2.390 and 2.416, average atomic radius between 1.062Å and 1.263 Å, average electronegativity between 2.227 and 2.414, average atomic number between 23.041 and 36.826, and average atomic molar mass between 246.031 g.mol^{-1} and 436.179 g.mol^{-1}.

Figure 2 shows that the average coordination number is not profoundly changed on each binary system and ternary section and when changing from Sb_2S_3-As_2S_3 to Sb_2Te_3-As_2S_3 system and from one ternary section to another with the increasing Sb_2Te_3 content from 10 mol% to 40 mol%.

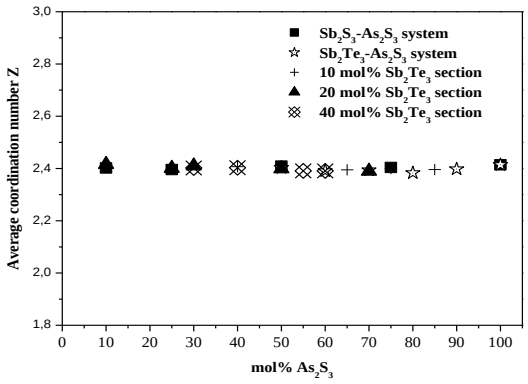

Fig. 2. Average coordination number (Z) of glasses as a function of As_2S_3 content.

The average coordination number (Z) for all the compositions studied is very close to 2.40 [7] and is therefore not dependent on the composition of the glasses. It can be considered as invariable. Invariability of Z was observed in $As_{40}Se_xTe_{(60-x)}$ [7], $As_{40}S_{(60-x)}Se_x$ (x = 0, 15, 30, 45 and 60) and $As_{24}S_{(76-y)}Se_y$ (y = 0,19,38, 57 and 76) glasses [8].

Figures 3, 4 and 5 show, respectively, that the average atomic radius (R_{av}), average atomic number (Z_{av}) and average atomic molar mass (M_{av}) of the compositions decrease on the binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and on the ternary sections containing 10, 20 and 40 mol% of Sb_2Te_3 in Sb_2S_3-As_2S_3-Sb_2Te_3 system with increasing As_2S_3 content.

Figures 3, 4 and 5 further indicate that the R_{av}, Z_{av} and M_{av} characteristics increase from the Sb_2S_3-As_2S_3 system to the Sb_2Te_3-As_2S_3 system and from the ternary section containing 10 mol% of Sb_2Te_3 to those containing 20 mol% and 40 mol% of Sb_2Te_3.

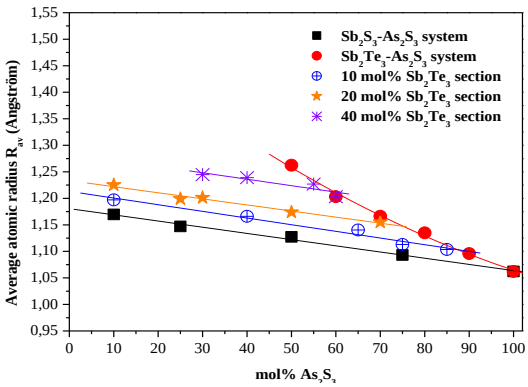

Fig. 3. Average atomic radius (R_{av}) of glasses as a function of As_2S_3 content on binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3).

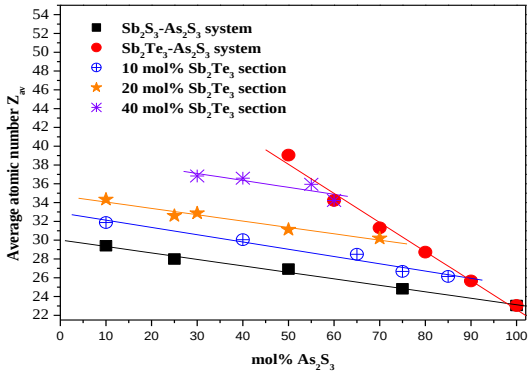

Fig. 4. Average atomic number (Z_{av}) of glasses as a function of As_2S_3 content on binary systems (As_2S_3-Sb_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3).

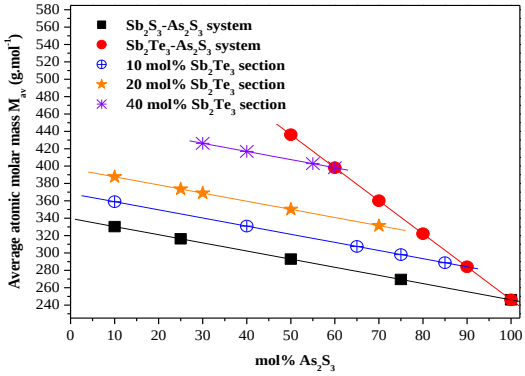

Fig. 5. Average atomic molar mass (M_{av}) of glasses as a function of As_2S_3 content on binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3).

Figure 6 shows that the average electronegativity (χ_{av}) increases on the binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and on the ternary sections (10, 20 and 40 mol% Sb_2Te_3) as the As_2S_3 content increases. χ_{av} decreases from the Sb_2S_3-As_2S_3 system to the Sb_2Te_3-As_2S_3 system and when moving from one ternary section (10 mol% of Sb_2Te_3) to another (40 mol% of Sb_2Te_3).

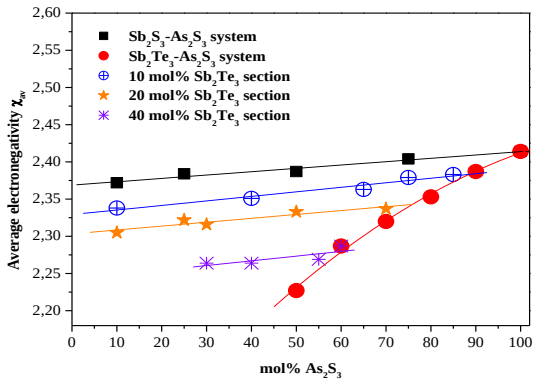

Fig. 6. Average electronegativity (χ_{av}) of glasses as a function of As_2S_3 on binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3.

4. Discussions

The X-ray powder diffractograms of the studied compositions of Sb_2S_3-As_2S_3-Sb_2Te_3 system (Figure 1) all show scattering halos characteristic of the glassy state. The materials synthesized in our study are glasses. They lack a long-range order contrary to their crystallized counterparts which are provided with it.

The observed differences between the experimental and theoretical atomic percentages obtained by EDS for the considered compositions (Tables 1-5) can be explained by the inevitable condensation of the volatile elements in the cold part of the silica tubes used to perform the syntheses. Despite these discrepancies, the samples of the different binary systems and ternary sections of the Sb_2S_3-As_2S_3-Sb_2Te_3 system have very close experimental and theoretical compositions. Thus, we can suggest that when a liquid (obtained by melting a material) gives rise to a glass by rapid cooling, the short-range order of the glass is the same as that of the liquid. This is because the structure of the liquid freezes during the transition from liquid to glass. Liquid and glass have similar composition and chemical formula.

The values of average coordination number (Z), average atomic radius (R_{av}), average atomic number (Z_{av}), average atomic molar mass (M_{av}) and average electronegativity (χ_{av}) in Tables 7-11 indicate the required values of these parameters for glass formation in the Sb_2S_3-As_2S_3-Sb_2Te_3 system. Outside the ranges of values indicated in these tables, the formation of glass in the above system is impossible under the synthesis conditions (rapid cooling of a liquid phase) adopted in this study.

The constancy of the average coordination number Z (Figure 2) indicates that the increase in the contents of As_2S_3 (on the binaries and ternary sections) and Sb_2Te_3 (from 10 mol% to 40 mol% in the ternary) does not influence this parameter. The invariability of Z is explained by the iso-structural substitution occurring on the one hand between the atoms of antimony (Sb) and arsenic (As) which have the same coordination number equal to 3 and on the other hand between the atoms of sulfur (S) and tellurium (Te) whose coordination is equal to 2. The average coordination number close to 2.4 suggests that the studied binary and ternary compositions of the Sb_2S_3-As_2S_3-Sb_2Te_3 system easily form glasses. The average coordination number being between 2 and 3 indicates that Sb_2S_3-As_2S_3-Sb_2Te_3 glasses are over-stressed or rigid materials according to [9]. The resulting structural arrangement of the units that make up the glasses is two-dimensional.

The overall decrease of R_{av} (Figure 3), Z_{av} (Figure 4) and M_{av} (Figure 5) and the growth of χ_{av} (Figure 6) as a function of As_2S_3 content on the binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3) of the Sb_2S_3-As_2S_3-Sb_2Te_3 system are due to the substitution:

- of Sb_2S_3 (high R_{av}, Z_{av} and M_{av} values equal to 1.18 Å, 30 and 339.715 $g.mol^{-1}$ respectively and low χ_{av}=2.368) by As_2S_3 (low R_{av}, Z_{av} and M_{av} values equal to 1. 062 Å, 23.041 and 246.039 $g.mol^{-1}$ and high value of χ_{av}=2.414) on the Sb_2S_3-As_2S_3 system and on the ternary sections containing 10, 20 and 40 mol% of Sb_2Te_3,

- of Sb_2Te_3 (high values of R_{av}, Z_{av} and M_{av} respectively equal to 1.42 Å, 51.6 and 626.32 $g.mol^{-1}$ and low value of χ_{av}=2.08) by As_2S_3 (low values of R_{av}, Z_{av} and M_{av} respectively equal to 1.062 Å, 23.041 and 246.039 $g.mol^{-1}$ and high value of χ_{av}=2.414) on the Sb_2Te_3-As_2S_3 system.

Thus, the decrease in R_{av} (Figure 3), Z_{av} (Figure 4), and M_{av} (Figure 5) allows one to suggest, respectively, that the average size of atoms, the average size of electron layers (or clouds), and the average atomic molar mass of a mole of the compositions are getting smaller and smaller. The growth of χ_{av} (Figure 6) indicates that the ability of atoms to attract electrons increases if they are engaged in a bond.

We can suggest, from the above, that the formation of glasses in the Sb_2S_3-As_2S_3-Sb_2Te_3 system is conditioned by an increase of the average electronegativity (χ_{av}) and a decrease of the average atomic size (R_{av}), of the average atomic number (Z_{av}) and of the average atomic molar mass (M_{av}) when the content of As_2S_3 increases on the binary systems and ternary sections of the said system.

Let us note that the decreases of R_{av}, Z_{av} and M_{av} observed above can be assimilated respectively to a decrease of the volume occupied by the atoms (since the atoms can be supposed spherical), to a shortening of the extent of the electronic layers reinforcing the coulombic force between the peripheral electrons and the nucleus (the peripheral electrons become less and less free because they are more and more under the influence of the nucleus) and to a decrease of the atomic molar mass of the compositions when the content of As_2S_3 increases on the binary systems and ternary sections.

The increase in R_{av} (Figure 3), Z_{av} (Figure 4) and M_{av} (Figure 5) and the decrease in χ_{av} (Figure 6) observed when moving from the Sb_2S_3-As_2S_3 system to the Sb_2Te_3-As_2S_3 system and from one ternary section to another, can be explained by:

- the substitution of Sb_2S_3 (low values of R_{av}, Z_{av} and M_{av} equal to 1.18 Å, 30 and 339.715 $g.mol^{-1}$ respectively and high value of χ_{av}=2.368) by Sb_2Te_3 (high values of R_{av}, Z_{av} and M_{av} equal to 1.42 Å, 51.6 and 626.32 $g.mol^{-1}$ respectively and low value of χ_{av}= 2.08) from the Sb_2S_3-As_2S_3 system to the Sb_2Te_3-As_2S_3 system,
- the addition of constant contents (10, 20 and 40 mol%) of Sb_2Te_3 to Sb_2S_3-As_2S_3 system to obtain the ternary sections.

Thus, the increase of R_{av}, Z_{av} and M_{av} from the Sb_2S_3-As_2S_3 system to the Sb_2Te_3-As_2S_3 system and from one ternary section to another respectively in Figures 3, 4 and 5 can be equated respectively to an increase:

- of the occupied volume (since the atoms can be assumed spherical) as R_{av} grows,
- of the extent of the electronic layers weakening the coulombic force between the peripheral electrons and the nucleus (the peripheral electrons become more and more free because they are less and less under the influence of the nucleus) because Z_{av} grows,
- and of the molar mass (as Mav increases) of the compositions when the Sb_2Te_3 content increases in the Sb_2S_3-As_2S_3-Sb_2Te_3 system.

The decrease in χ_{av} (Figure 6) indicates an overall decrease in the ability of the atoms to attract electrons when forming bonds.

From the above interpretations, we can suggest that the increase in R_{av}, Z_{av} and M_{av} and the decrease in χ_{av} due to Sb_2Te_3 do not affect the nature of the obtained materials because the results of this study indicate that the compositions prepared are glasses. Even if the average electronegativity (χ_{av}) decreases, the average electropositivity (ability to give up electrons) that may increase does not predominate over the average electronegativity in these materials because they remain glassy.

Among the compounds constituting Sb_2S_3-As_2S_3-Sb_2Te_3 system, As_2S_3 is the excellent glass former by forming glass alone by a conventional quenching method [1], Sb_2S_3 has a poor glass-forming ability [10] and Sb_2Te_3 does not form glass by a conventional quenching method [1]. We can suggest that the increasing or the decreasing of the studied parameters (R_{av}, χ_{av}, Z_{av} and M_{av}) when the content of As_2S_3 increases can be related to the increasing of glass-forming ability of binary and ternary glasses in Sb_2S_3-As_2S_3-Sb_2Te_3 system. This is due to the covalent character of As_2S_3 which has As-S type covalent bonds.

The decrease or increase of these parameters when the Sb_2Te_3 content increases from 10 mol% to 40 mol% in the Sb_2S_3-As_2S_3-Sb_2Te_3 system can be assimilated to a decrease of the vitrification ability because of the semi-metallic character of Sb_2Te_3 which is materialized by the Sb-Te bonds.

5. Conclusions

This study has been realized on several glasses belonging to binary systems (Sb_2S_3-As_2S_3 and Sb_2Te_3-As_2S_3) and a series of three sections in Sb_2S_3-As_2S_3-Sb_2Te_3 system where glasses have constant concentrations of Sb_2Te_3 at 10 mol%, 20 mol% and 40 mol%.

The existence of the scattering halos on the X-ray powder diffractograms of the compositions of the Sb_2S_3-As_2S_3-Sb_2Te_3 system showed that the materials synthesized during our study are glasses (lacking a long-range order).

Despite the slight differences between the experimental and theoretical atomic percentages due to the EDS results, we can suggest that the initial compositions of the Sb_2S_3-As_2S_3-Sb_2Te_3 system which gave rise to the glasses during the rapid cooling of their liquid phases have chemical formulas close to those non-crystalline materials.

It has shown dependence of average electronegativity (χ_{av}), average atomic size (R_{av}), average atomic number (Z_{av}) and average atomic molar mass (M_{av}) of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses on As_2S_3 and Sb_2Te_3 contents except average number of coordination (Z).

The behaviours of the above parameters (χ_{av}, R_{av}, Z_{av} and M_{av}) have been discussed in term of bond changes due (i) on the one hand to the replacement of Sb_2S_3 by As_2S_3 in Sb_2S_3-As_2S_3 system and ternary sections (containing 10, 20 and 40 mol% of Sb_2Te_3) and on the other hand to the replacement of Sb_2Te_3 by As_2S_3 in Sb_2Te_3-As_2S_3 system when the content of As_2S_3 increases (ii) to the increase in Sb_2Te_3 concentration from 10 mol% to 40 mol% section in Sb_2S_3-As_2S_3-Sb_2Te_3 ternary system.

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