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INVESTIGATION OF ANTIMONY LOCAL ENVIRONMENT IN SOME Sb_2S_3-As_2S_3-Sb_2Te_3 GLASSES BY MÖSSBAUER SPECTROSCOPY

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Some glasses with Sb_2Te_3 constant concentrations at 0, 20 and 40 mol% in Sb_2S_3-As_2S_3-Sb_2Te_3 system have been studied by means of ^{121}Sb Mössbauer spectroscopy. Mössbauer parameters such as the isomer shift (δ), the quadrupolar interaction (Δ) and the linewidth (Γ) have been used to investigate the local environment of 121 antimony concerning its oxidation state, its coordination, the nature of the chemical bonding in the polyhedron coordination and the stereochemical activity of the non-bonded pair called E. The interpretation of the results has indicated that the negative values of isomer shift (δ) are characteristic of pyramidal environments (SbS_3E) in all studied cases. The increase in δ as the function of As_2S_3 content has been attributed to an increasing of Sb-S covalency bonds in SbS_3E pyramidal units. The length of Sb-S bonds decreased and became short. The increasing of Δ in the cases of Sb_2S_3-As_2S_3 system and 20 mol% Sb_2Te_3 section in Sb_2S_3-As_2S_3-Sb_2Te_3 system has indicated an increase in the stereochemical activity of antimony atom's lone pair. The decrease in Δ for glasses of 40 mol% Sb_2Te_3 section has induced a decreasing of the stereochemical activity of the lone pair and the covalency of Sb-S bonds in these suggested case.

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1. Introduction

Glass forming region is found to be wide in the Sb_2S_3-As_2S_3-Sb_2Te_3 [1] system. Thermal and optical properties of glasses at Sb_2Te_3 constant concentrations of 0, 20 and 40 mol% in the glass region of the above system, have indicated that these properties do not have the same behaviour when the composition of the glasses varies with the increasing of As_2S_3 content [1]. Estimation of glass-forming ability and glass stability by thermal properties in the same system has shown that these glasses can be obtained easily and become most stable against crystallization when the content of As_2S_3 increases [2]. The partial replacement of Sb_2S_3 (less covalent) by As_2S_3 (covalent) in each proposed case of Sb_2S_3-As_2S_3-Sb_2Te_3 system, can exhibit a predominantly character by involving probably the formation of high stable network structure which may be due to the presence of covalent bonding. That means that, As_2S_3 acts to increase the homogeneity of the glasses, the strength of the glass network and the covalence character by forming stable units which insure effectively the stability of the glasses [2].

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According to modern concepts, the atoms constituting the structural network of homogeneous chalcogenide vitreous semiconductors donate all of their valence electrons to form bonds with the neighbouring atoms (8-N). By using Mössbauer spectroscopy, the validity of these concepts has been confirmed in glasses of Sb_2S_3-As_2S_3-Tl_2S [3] and Sb_2Se_3-As_2Se_3-Sb_2Te_3 [4] systems where antimony exists only as Sb^{III} species in the studied glasses. According to Leh et al. [4] its coordination is $SbSe_3E$ and E being the 5s nonbonding electrons. Arsenic usually obeys the (8-N) rule, which means that its coordination number is determined by the number needed to complete its valence shell. Arsenic is therefore found in a in a pyramidal AsS_3E-type environment [3].

The present paper is devoted first to complete the previous studies [1,2] by the study of Sb environment in some Sb_2S_3-As_2S_3-Sb_2Te_3 glasses using the Mössbauer spectroscopy and second to verify if the above atom has the same oxidation state like antimony atoms in studied systems [3, 4].

2. Experimental

2. 1 Synthesis of glasses

Synthesis of binary Sb_2S_3-As_2S_3 glasses and that of 20 mol% and 40 mol% Sb_2Te_3 sections in the Sb_2S_3-As_2S_3-Sb_2Te_3 system were previously described [1-2].

2. 2 Measure of ^{121}Sb Mössbauer spectroscopy

Mössbauer spectroscopy is a recoil-free emission absorption resonance of γ rays. It is used to characterize the electronic environment around antimony (Sb), the probed atom (in our case). The ^{121}Sb Mössbauer measurements were carried out in standard transmission geometry using as γ source the ^{121m}Sn isotope include in a $BaSnO_3$ matrix.

The source and the absorber were cooled down simultaneously to liquid helium temperature in order to increase the recoil-free absorption's fraction and emission processes. The calibrated velocity scale obtained with the standard spectrum of an iron absorber was done by using a ^{57}Co source. The zero isomer shift was defined from the spectrum of the reference InSb (-8.70 mm/s relative to the $BaSnO_3$ source).

3. Results

Glasses containing 10, 50 and 75 mol% As_2S_3 in the Sb_2S_3-As_2S_3 system, those of 20 mol% section with 30, 60 and 80 mol% As_2S_3 and glasses of 40 mol% Sb_2Te_3 section with 25, 40 and 60 mol% As_2S_3 in Sb_2S_3-As_2S_3-Sb_2Te_3 system have been investigated.

Examples of ^{121}Sb Mössbauer absorption spectra of the studied glasses (0, 20 and 40 mol% Sb_2Te_3 sections) in the Sb_2S_3-As_2S_3-Sb_2Te_3 system are shown in Fig. 1.

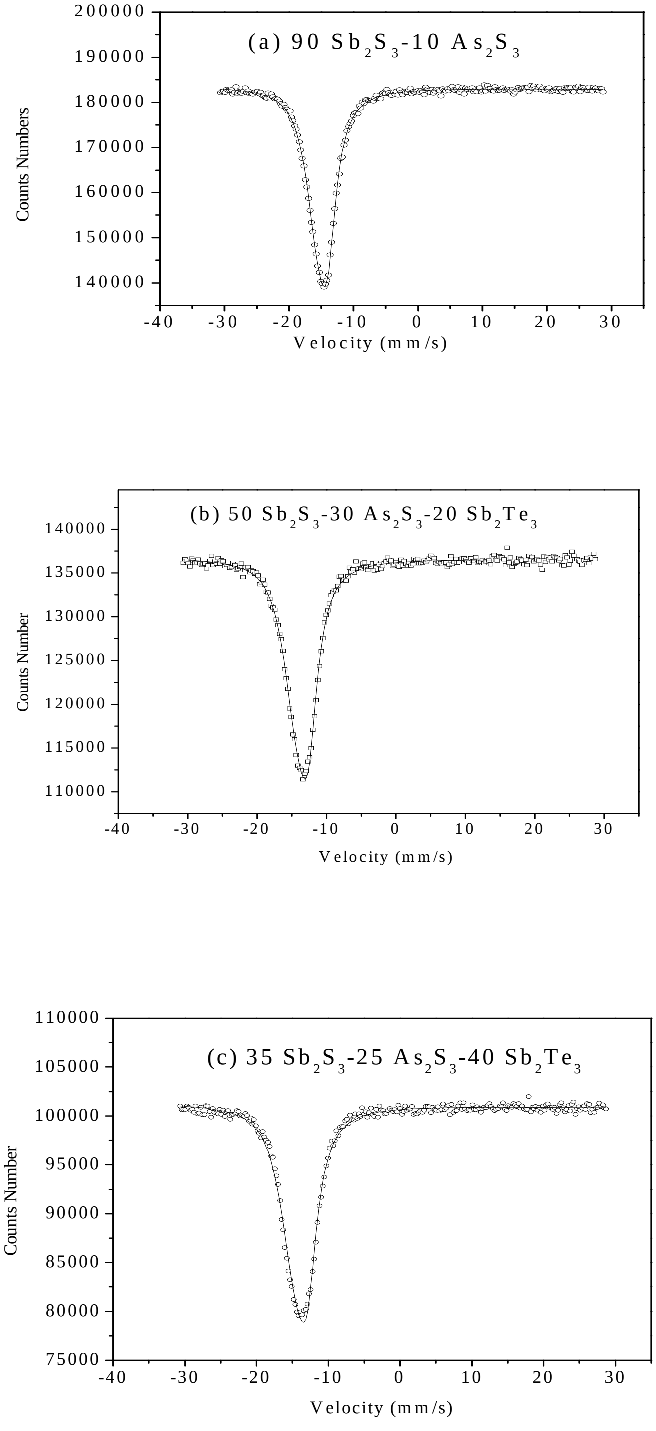

Fig. 1. ^{121}Sb-Mössbauer absorption spectra of (a) 90%Sb_2S_3-10%As_2S_3, (b) 50%Sb_2S_3-30%As_2S_3-20%Sb_2Te_3 and (c) 35%Sb_2S_3-25%As_2S_3-40%Sb_2Te_3 glasses

The peak sight of Mössbauer spectra is not function of the glasses composition because all spectra of studied glasses in Sb_2S_3-As_2S_3-Sb_2Te_3 system which show only one peak are large asymmetric lines. That indicates the presence of the electric field gradient inducing the interaction of the absorption line in an octet [4]. However, the asymmetry of the Mossbauer spectrum allows a determination of the sign of the electric-field gradient [5]. Generally, for Sb, the eight lines are unresolved. Goodness of fits was checked as it is shown by the χ^2 values and misfit (table 1) taking into account in each case, only one hyperfine site for Sb without the asymmetric parameter (η). The presence of one peak in Mössbauer spectra of glasses has been observed in Sb_2Se_3-As_2Se_3-Sb_2Te_3 (at 10 mol% Sb_2Te_3) by Leh et al. [4], AgI-Sb_2S_3 and Ag-As-Sb-Se systems by Bychkov and Wortmann [6], Ge-Sb-S by Skordeva et al. [7] and Sb_2S_3-As_2S_3-Tl_2S by Durand et al. [3].

The hyperfine interaction parameters of glasses such as isomer shift (δ), quadrupole coupling (Δ) and linewidth (Γ) calculated from the analysis of the different Mössbauer spectra are given (table 1).

Table 1. Summary of isomer shift (δ), quadrupolar interaction (Δ), linewidth□□□□□ (Γ), χ^2 and misfit□ resulting from the analysis of Mössbauer spectra of 0, 20 and 40 mol% Sb_2Te_3 sections in Sb_2S_3-As_2S_3-Sb_2Te_3 system.

Sb_2Te_3 sections	Mol% As_2S_3	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	χ^2	Misfit (%)
0 % Sb_2Te_3	10 % As_2S_3	- 6.15 (1)	+ 9.0 (2)	1.60 (4)	1.16	0.017
	50 % As_2S_3	- 4.84 (1)	+ 12.1 (2)	1.77 (5)	1.49	0.101
	75 % As_2S_3	- 4.64 (2)	+ 12.0 (3)	1.42 (7)	1.22	0.102
20 % Sb_2Te_3	30 % As_2S_3	- 4.86 (1)	+ 10.5 (3)	1.62 (6)	1.27	0.069
	60 % As_2S_3	- 4.83 (1)	+ 11.3 (2)	1.45 (4)	1.54	0.079
	80 % As_2S_3	- 4.73 (1)	+ 11.8 (2)	1.35 (5)	1.23	0.068
40 % Sb_2Te_3	25 % As_2S_3	- 5.25 (1)	+ 10.9 (2)	1.71 (5)	1.95	0.229
	40 % As_2S_3	- 4.96 (2)	+ 10.1 (3)	1.65 (6)	1.28	0.107
	60 % As_2S_3	- 5.15 (2)	+ 9.5 (4)	1.97 (7)	1.95	0.496

Uncertainties in the last digit(s) of the Mössbauer parameters (δ, Δ and Γ) are given in parentheses.

Three trends of linewidth (Γ) can be observed for studied glasses of Sb_2S_3-As_2S_3-Sb_2Te_3 (fig. 2).

In the case of Sb_2S_3-As_2S_3 glasses, Γ increases from 1.60 mm/s (25% As_2S_3) to 1.77 mm/s (50% As_2S_3) and decreases from the latter value to 1.42 mm/s (75% As_2S_3). The linewidth (Γ) decreases continuously from 1.62 mm/s to 1.35 mm/s when As_2S_3 content increases from 30% to 80% for 20 mol% Sb_2Te_3 section in Sb_2S_3-As_2S_3-Sb_2Te_3 system. The linewidth (Γ) decreases (1.71 mm/s to 1.65 mm/s) when the As_2S_3 content increases from 25 mol% to 40 mol%. An optimal value of linewidth (Γ) (1.97 mm/s) is observed when the content of As_2S_3 is equal to 60% for 40 mol% Sb_2Te_3 section of Sb_2S_3-As_2S_3-Sb_2Te_3 system. The substitution of Sb_2S_3 by As_2S_3 has an influence on the linewidthΓ's values.

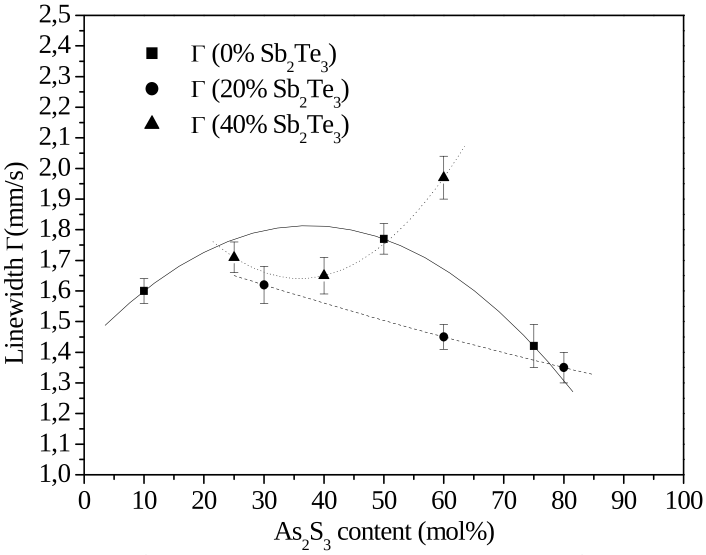

Figure 2 : Variation of the linewidth with the As_2S_3 concentration of the 0, 20 and 40 mol% Sb_2Te_3 sections in Sb_2S_3-As_2S_3-Sb_2Te_3 system.

The isomer shift (δ) has negative values as indicated in table 1. For δ of studied Sb_2S_3-As_2S_3-Sb_2Te_3 glasses, two trends are observed as indicated in Fig. 3:

(i) δ increases from -6.15 mm/s (10% As_2S_3) to -4 .46 mm/s (75% As_2S_3) for Sb_2S_3-As_2S_3 glasses and from -4.86 mm/s (30% As_2S_3) to -4.73 mm/s (80% As_2S_3) for 20 mol% Sb_2Te_3 section in Sb_2S_3-As_2S_3-Sb_2Te_3 system with increasing mol% As_2S_3 in both series of glasses,

(ii) δ increases from -5.25 mm/s (25% As_2S_3) to -4.96 mm/s (40% As_2S_3) but decreases and has a value equal to -5.15 mm/s belonging to the binary glass of Sb_2Te_3-As_2S_3 system with 60 mol% As_2S_3.

In spite of the observed different behaviours of δ, the effect of substituting Sb_2S_3 by As_2S_3 (or vis-versa) is to change really δ in all studied cases. In Sb_2S_3-As_2S_3 system, the glass with 10 mol% As_2S_3 admits δ=-6.15 mm/s which is near the isomer shift of crystalline Sb_2S_3 (δ=-6.19 mm/s) determined by Durand et al. [3].

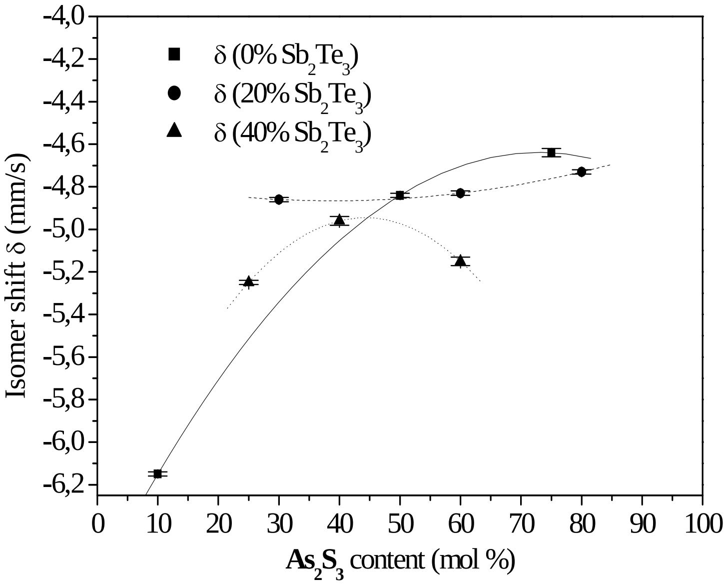

Figure 3 : Composition dependence of the isomer shift δ for Sb_2S_3-As_2S_3-Sb_2Te_3 glasses at constant Sb_2Te_3 concentrations of 0, 20 and 40 mol%

The quadrupolar interaction (Δ=eQVzz) has positive values for all the alloys as indicated in table 1. Since eQ for ^{121}Sb is negative, the sign of the principal component of the electric-field gradient Vzz is negative in all cases. This situation is typical for crystalline and amorphous chalcogenides and chalcohalides of antimony except for telluride compounds [8-14] and indicates that the direction z of the principal component of the electric-field gradient is determined by the direction of the lone electron pair of Sb^{III} containing an excess of p electron density.

Figure 4 shows the evolution of Δ versus mol% As_2S_3. It indicates the increase in Δ from 9 mm/s (10 mol% As_2S_3) to 12.1 mm/s (50 mol%As_2S_3) in Sb_2S_3-As_2S_3 system. But Δ of the glass with 75 mol% As_2S_3 equal to 12 mm/s is similar to that of the glass with 50 mol% As_2S_3 (Δ=12.1 mm/s) but is higher than that of glass with 10 mol% As_2S_3. Δ increases and decreases monotonically with As_2S_3 mol% from 10.5 mm/s (30% As_2S_3) to 11.8 mm/s (80% As_2S_3) and from 10.9 mm/s (25% As_2S_3) to 9.5 mm/s (60% As_2S_3) respectively on 20 mol% Sb_2Te_3 section and 40 mol% Sb_2Te_3 section of Sb_2S_3-As_2S_3-Sb_2Te_3 system. So the increasing or decreasing of Δ depends on the studied glasses composition. Figure 4 also indicates that, for As_2S_3 content higher than 30 mol%, Δ decreases from 0 mol% Sb_2Te_3 to 20 and 40 mol% Sb_2Te_3 sections in Sb_2S_3-As_2S_3-Sb_2Te_3 system.

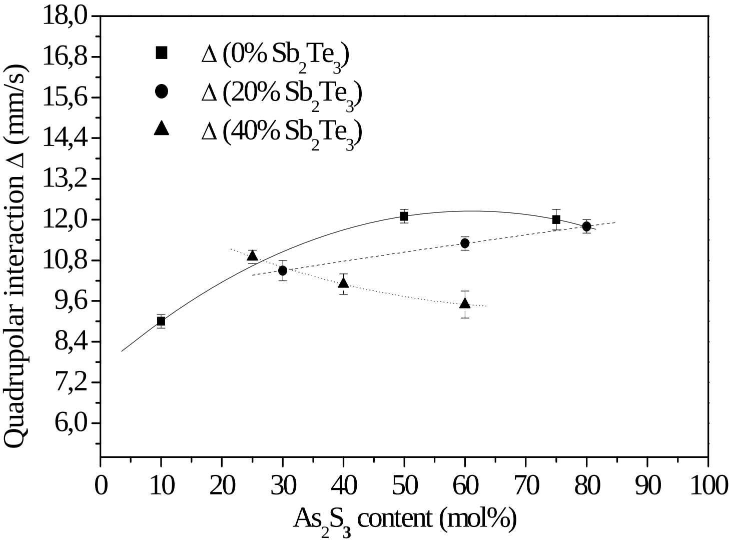

Figure 4 : Composition dependence of the quadrupolar interaction Δ for Sb_2S_3-As_2S_3-Sb_2Te_3 glasses at constant Sb_2Te_3 concentrations of 0, 20 and 40 mol%

4. Discussions

The linewidth (Γ) is a direct function of the lifetime of the excited state by the relation $\Gamma \leq \hbar/t$ with $t = t_{1/2} \ln 2$ [4]. The values of linewidth being between 1.16 and 1.95 mm/s are lower than the natural emission line of antimony (2.10 mm/s). This can allow us to suggest that the antimony atom has one environment type in the studied Sb_2S_3-As_2S_3-Sb_2Te_3 glasses.

Generally the isomer shift δ gives the information on the electron density of the nucleus (oxidation state), the coordination and the nature of the chemical bonding. The negative values of δ observed in table 1 are characteristics for Sb (III) species [15]. In this case, antimony atom is in its lower oxidation state (III) like antimony atom in different systems studied [3, 4] and has a non-bonded pair ($5s^2$) called E. In other words, antimony (Sb) atoms constituting the structural network of the chalcogenide glasses with arsenic (As), sulphur (S) and tellurium (Te) donate all of their valence electrons of p-atomic orbital to form bonds with their neighbouring atoms. The isomer shift's values are characteristic of pyramidal environments (SbS_3E). The increasing of δ with mol% As_2S_3 in Sb_2S_3-As_2S_3 system, 20 mol% Sb_2Te_3 section and 40 mol% Sb_2Te_3 section (for glasses with 25 and 40 mol% As_2S_3) of Sb_2S_3-As_2S_3-Sb_2Te_3 system, induces a decrease in the s-electron density of antimony atom. There is a linear relation between the isomer shift and the electron density. The evolution of the two parameters (δ and electron density) can be interpreted as an increasing of Sb-S covalency bonds. In other words, the increase of δ can be attributed to the decrease of Sb-S bonds length in the SbS_3E pyramidal environments. Therefore Sb-S bonds become short. This has been observed by Leh et al [4] in 10 mol% Sb_2Te_3 section of Sb_2Se_3-As_2Se_3-Sb_2Te_3 system where a decrease of the s electron at the Sb nucleus has been attributed to the decrease of the Sb-Se bond length. In the Sb_2S_3-As_2S_3 system, the decrease of the isomer shift with increasing Sb_2S_3 concentration can be attributed to the increase of the mean Sb-S bond length in the SbS_3E pyramidal environments [3]. The s-electron density of antimony atoms, being related directly to the covalency of Sb-S bonds formation, the increase in isomer shift indicates a slight decrease in Sb-S bonds ionicity. So a decreasing of Sb-S distance induces the formation of pyramidal SbS_3E coordination of antimony. Sb-S bonds become more covalent when As_2S_3 content increases.

The decreasing of δ observed from ternary glass of 40 mol% Sb_2Te_3 section of Sb_2S_3-As_2S_3-Sb_2Te_3 system to the binary one (with 60 mol% As_2S_3) of Sb_2Te_3-As_2S_3 system indicates an increase in s-electron density of antimony atom. This behaviour has been observed in two glasses of Ge-Sb-S system [7]. According to Lippens [16], the decreasing of δ is related to the increase in the number of Sb s electrons, and /or to the decrease in the number of Sb 5p electrons. The decrease in δ can be also due to the absence of Sb_2S_3 in the binary glass. In this case, the covalency of Sb-S bonds (which become long) decreases and the s-electron density increases. This can enable one to suggest that the decreasing of δ, in this case, can be related to the differences in the local geometry of SbS_3E units in the binary and ternary glasses. The low value of δ for the vitreous composition (with 10 mol% As_2S_3 in the Sb_2S_3-As_2S_3 system) observed above, is probably due to the high content of Sb_2S_3 (90 mol %). It can be also correlated to Stevens and Bowen [8] observation that the isomer shift for amorphous antimony (III) sulphide is larger than that of crystalline stibnite Sb_2S_3. This was explained by the shorter Sb-S distances in the amorphous material. The s-electron density at the Sb nucleus of this glass is higher than that of its counterparts of Sb_2S_3-As_2S_3 system. It is also higher than that of Sb_2S_3-As_2S_3-Sb_2Te_3 glasses (20 mol% and 40 mol% Sb_2Te_3 sections). The observations can enable one to suggest that, even if all studied glasses contain SbS_3E pyramidal polyhedron, the Sb-S distance differs. It means that the Sb-S bond length in SbS_3E pyramidal environments of glass with 10 mol% As_2S_3 in Sb_2S_3-As_2S_3 system is less than that of its counterparts of the aforesaid system and that of glasses belonging to 20 mol% and 40 mol% Sb_2Te_3 sections in Sb_2S_3-As_2S_3-Sb_2Te_3 system.

The quadrupolar interaction (Δ) is an indicator of the asymmetric of the electron distribution around the Sb atoms. This occurs for strongly distorted octahedral when $\Delta>0$ [15]. It also characterizes the stereochemical activity of E [3, 15] which is said to increase with the distortion of the coordination polyhedron (or trigonal pyramids). The increasing of Δ in the case of Sb_2S_3-As_2S_3 system and 20 mol% Sb_2Te_3 section in Sb_2S_3-As_2S_3-Sb_2Te_3 system indicates an increase in the stereochemical activity of the lone pair and the distortion of the trigonal pyramid (SbS_3E) units when As_2S_3 content increases. This induces that the environment of antimony atom is more distorted (or asymmetrical) because of the important stereochemical activity of the lone-pair E with probably the loss of its sphericity. A strong asymmetry of the electron density around the Sb nucleus, as expected with 3-fold coordination can be suggested. As_2S_3 strengths the covalent character by increasing the distortion of antimony's environment. The comparison of different values of Δ in Sb_2S_3-As_2S_3 system and 20 mol% Sb_2Te_3 section enables one to suggest that the covalent character of Sb-S bonds in glasses (with high mol% As_2S_3) is higher than that of Sb-S bonds in glasses (with low mol% As_2S_3). The stereochemical activity of the lone pair of the first glasses is more important than that of the second type of glass. The antimony environment is more distorted so more asymmetrical.

The decrease in Δ for glasses of 40 mol% Sb_2Te_3 section and when the concentration of Sb_2Te_3 increases from 0 mol% Sb_2Te_3 section to 20 mol% and 40 mol% Sb_2Te_3 sections of Sb_2S_3-As_2S_3-Sb_2Te_3 system (for As_2S_3 content ≥ 30 mol%) indicates or induces a decreasing of the electron density around the Sb nucleus. This electron density is not more asymmetric because the antimony's environment is less distorted. The stereochemical activity of the lone pair decreases. The covalent character decreases in these suggested cases. This implies the decrease in the covalency of Sb-S bonds. The distortion of the coordination polyhedron (here the trigonal pyramid) decreases.

5. Conclusions

Local environment of 121 antimony atom in some Sb_2S_3-As_2S_3-Sb_2Te_3 glasses has been investigated by means of Mössbauer spectroscopy. It has been possible by following the variations of the Mössbauer parameters such as the isomer shift (δ), the quadrupolar interaction (Δ) and the linewidth (Γ) to show that: (i) the negative values of δ are characteristics of Sb (III) species. That means the antimony atom has its lower oxidation state (III) and has a non-bonded pair ($5s^2$) called E. So antimony has a pyramidal environment (SbS_3E). The increase in δ with the content of As_2S_3 has been correlated to a decrease of s-electron density at this nucleus, inducing an increase of the covalency. Sb-S bonds in this case become short; (ii) the increasing of Δ in binary and ternary glasses indicates an increase in the stereochemical activity of the lone pair when As_2S_3 content increases. This is due to the important stereochemical activity of the lone pair by inducing that the environment of antimony atom is more distorted (or asymmetrical). The increasing of As_2S_3 content increases the strengths of the covalent bonds of the glasses by increasing of antimony environment. The covalent character increases. When the content of Sb_2Te_3 increases from 0 to 40 mol%, the stereochemical activity of the lone pair E and the covalent character decrease because Δ decreases. The environment of antimony atom is less distorted.

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