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Structural approach of Ge-X, GeX₂-Ag₂X (X=S,Se) glassy systems

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Abstract:

This paper presents a summary of our structural results obtained from X-ray Absorption Spectroscopy, Anomalous Wide Angle X-ray Scattering and Small Angle X-ray scattering for germanium chalcogenide glasses. At first, the local and the medium range order existing in the structure of GeX_x ($1.5 \leq x \leq 9$ and X=S,Se) binary glasses have been determined. Then, the results obtained for (1-y)GeX₂ + yAg₂X ternary glasses are presented.

1. INTRODUCTION:

The Ag-Ge-X (X = S, Se) germanium chalcogenide glasses present an interesting Ag⁺ ionic conduction property at room temperature. This physical property has been well characterized for these glasses in our laboratory [1], but the fundamental mechanisms of the ionic transport process are not yet fully understood from a microscopic point of view. This is partly due to the fact that the structure of these glasses is still not completely established, particularly in the Medium Range Order (M.R.O). For this reason, a structural approach of these germanium chalcogenide glasses has been undertaken.

All the previous works have demonstrated that germanium sulfide and selenide glasses present important structural analogies. At first, a comprehensive knowledge of GeX_x (X=S, Se and $1.5 \leq x \leq 9$) binary glasses is essential to be able then to follow the structural changes induced by the addition of a glassy network modifier: Ag₂X (X=S, Se).

An X-ray Absorption Spectroscopy (X.A.S.) study, made at room and low temperatures, has allowed us to determine the local surroundings of germanium, chalcogen and silver atoms in Ge-X binary and GeX₂ - Ag₂X (X=S, Se) ternary glasses. The Short Range Order (S.R.O.) study has been then completed by Anomalous Wide Angle X-ray Scattering (A.W.A.X.S.) measurements which allow us to confirm, first, the XAS results and then to extend M.R.O. characterization to 5 - 6 Å. Two binary GeS₃ and GeSe₃ glassy compositions have been analysed by AWAXS, the ternary glass study is in progress.

Finally, a more "macroscopic" structural approach has been made by using Small Angle X-ray Scattering (S.A.X.S.) in order to check the homogeneity of the binary and ternary glasses in a range 10 to 1000Å.

In this paper, we present our main structural conclusions for Ge-X and GeX₂-Ag₂X glassy systems obtained from X.A.S., A.W.A.X.S. and S.A.X.S. experiments made at LURE (ORSAY).

2. GeX_x (X=S,Se) GLASS FORMERS:

a) EXAFS results:

The EXAFS experiments, made at room temperature, have allowed us to characterize the first coordination spheres of chalcogen and germanium atoms in binary glasses [2-4] using αGeX₂, Ge and X=S or Se crystalline phases as structural references. In the whole glassy range, our results are in agreement with the 4-2 coordinated network (fourfold Ge and twofold X-sites). For (g)GeX₂ stoichiometric glass, homopolar bonds have not been found, but when the atomic composition moves off the GeX₂ one, the homopolar bond proportion increases: Ge-Ge bonds for Ge enriched glasses ($x < 2$)

and X - X bonds for chalcogen enriched compositions ($x > 2$), figure 1. This result supports the idea that the formation of these binary glasses is controlled by a chemically ordered process in agreement with the chemically ordered network model [5].

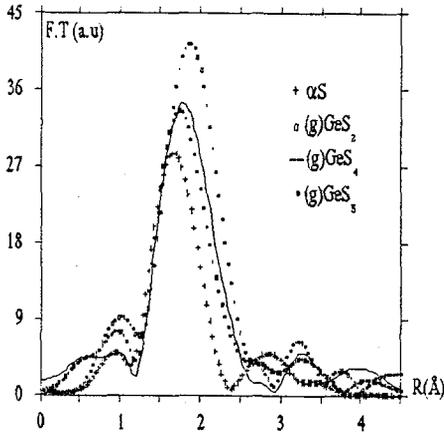


Figure 1: $k^2\chi(k)$ Fourier transform moduli, obtained from the S K-edge EXAFS study for S-enriched GeS_x glasses ($x \geq 2$) compared with the αS one.

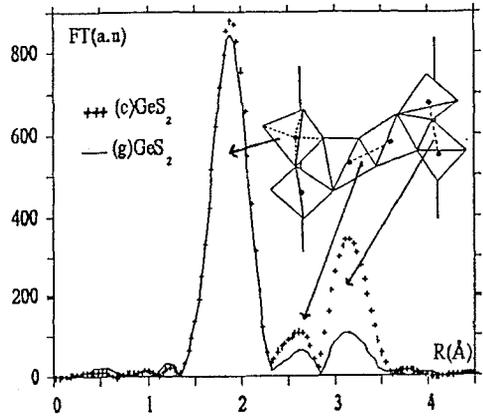


Figure 2: $k^2\chi(k)$ F.T. moduli obtained from the Ge K-edge EXAFS study for $(g)GeS_2$ and αGeS_2 which are related to αGeS_2 crystalline structure.

Low temperature Ge K-edge EXAFS experiments have been undertaken to decrease the thermal motion and thus weaken the Debye Waller factor values [6]. From this process, 35K spectra of sulfide glasses have allowed us to characterize the first three Ge coordination shells. It can be demonstrated that the Ge surroundings of $(g)GeS_2$ are very similar to those encountered in the crystallized high temperature form αGeS_2 [7], taken as structural reference, figure 2. In αGeS_2 , Ge is located in a regular tetrahedral site ($4Ge-S = 2.22\text{\AA}$). The crystalline structure is built up from $[GeS_3]_n$ chains of GeS_4 corner sharing tetrahedra, these chains themselves are connected by GeS_4 edge sharing tetrahedra to form layers, figure 2. Thus, for $(g)GeS_2$, the first Ge coordination is constituted by the tetrahedral surrounding of germanium by sulfur. The second shell sphere is due to short $Ge-Ge$ interactions of edge sharing tetrahedra (2.92\AA) and the third one corresponds to long $Ge-Ge$ interactions of corner-sharing tetrahedra (3.405\AA). These results are in accordance with the "outrigger raft" model [8, 9] which considers that $(g)GeX_2$ ($X=S, Se$) structures are mainly constituted by two-dimensional clusters based on GeX_2 crystalline network.

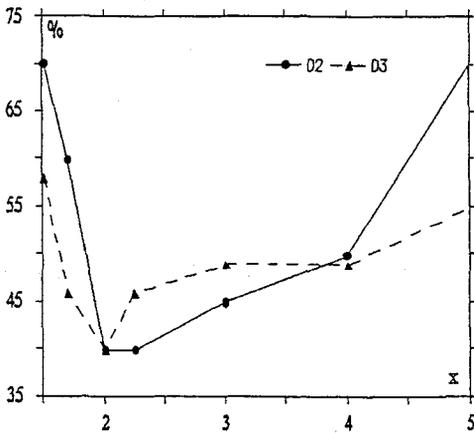


Figure 3: Depolymerization percentage of edge (D2) and corner (D3) sharing GeS_4 tetrahedra versus the GeS_x ($1.5 \leq x \leq 5$) glassy composition.

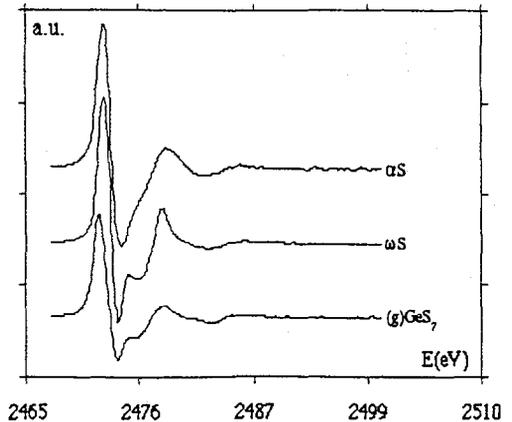


Figure 4: αS and ωS derivative XANES curves obtained at the S K-edge compared to that of a sulfur enriched binary glass, GeS_7 .

In addition, the Ge atom numbers in the glasses, $N_g(\text{Ge})$ obtained from EXAFS analysis [6] for the second (short Ge...Ge interactions) and the third coordination shells (long Ge...Ge interactions) of the glasses can be used to estimate the degree of depolymerization, D , of edge and corner sharing tetrahedra referred to αGeS_2 and to its Ge atom numbers $N_\alpha(\text{Ge})$. For (g)GeS₂, these breaking fractions $D = [N_\alpha(\text{Ge}) - N_g(\text{Ge})] / N_\alpha(\text{Ge})$ are both equal to $40 \pm 5\%$. For all the GeS_x glasses the existence of edge and corner sharing tetrahedra has been shown. Nevertheless, when the atomic composition varies from the GeS₂ one, the degree of depolymerization of corner and edge sharing tetrahedra increases significantly inducing an augmentation of the structural distortion in the intermediate range order (3-4Å). This increase of tetrahedra depolymerization is certainly due to the high homopolar bond proportion leading to the formation of Ge₂S₆ units for Ge enriched glasses or [S]_n chains for S enriched compositions. Moreover, the hypothesis of the existence of short [S]_n chains or screws rather than S₈ rings has been confirmed from S K-edge X-ray Absorption Near Edge Structures (XANES) study [4]. Indeed, the S K-edge XANES spectra of high S content glasses present resonance peaks (due to multiple scattering effects in the M.R.O.) very similar to those of the polymerized ω sulfur form [10], while the crystalline αS one (S₈ rings) is significantly different, figure 4.

b) AWAXS characterisation:

In order to complete S.R.O. description, an AWAXS analysis has been made on selenide glasses (sulfur K-edge is not accessible by this technique). The GeSe₃ and GeSe₅ compositions have been chosen to follow the structural changes occurring on both sides of the percolation edge suggested to exist around GeSe₄ composition. The Differential Distribution Functions of both Ge and Se atoms (DDF_{Ge} and DDF_{Se}), which specify respectively Ge and Se surroundings, have been extracted for GeSe₃ and GeSe₅ glasses (figures 5 and 6).

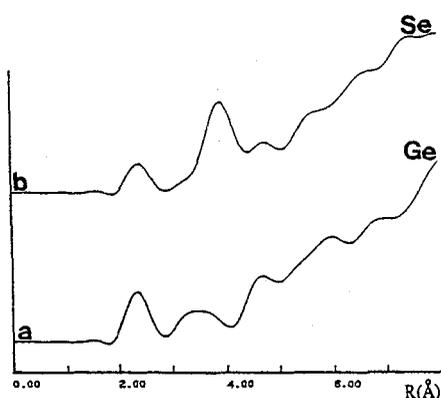


Figure 5: DDF_{Ge} (a) and DDF_{Se} (b) for GeSe₃.

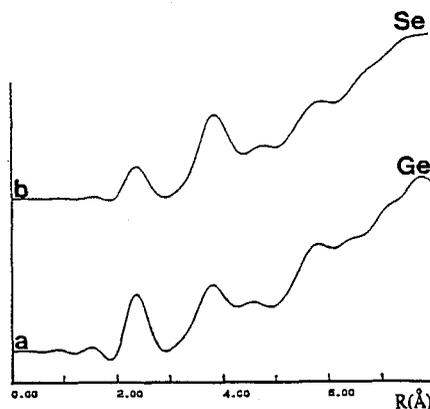


Figure 6: DDF_{Ge} (a) and DDF_{Se} (b) for GeSe₅.

These experimental DDF_{Ge} and DDF_{Se} curves, have been fitted until 5Å using gaussian distribution functions, taking into account the q dependance ($q = 4\pi \sin\theta / \lambda$) of the ponderation factor. The errors made on the structural parameters obtained from these simulations are around 15-20% of the coordination numbers, N , and about $\pm 0.02\text{Å}$ for the interaction lengths, R .

-For (g)GeSe₃, the DDFs curves (figure 5) were modeled using as structural basis the GeSe₂ crystalline network which is isomorphic with the αGeS_2 one. Indeed, the first sharp peak of DDF_{Ge} (figure 5-a) characterizes the tetrahedral surroundings of germanium by selenium ($N=3.95$, $R=2.35\text{Å}$). The second extended peak is mainly due to short ($N=0.35$, $R=3.02\text{Å}$) and long ($N=1.6$, $R=3.52\text{Å}$) Ge...Ge interactions of edge and corner sharing GeSe₄ tetrahedra. These results and the corresponding Ge-Se-Ge breaking fractions are consistent with the EXAFS results obtained for sulfide glasses. Nevertheless, the addition of Ge...Se interactions ($N=2.7$, $R=3.45\text{Å}$) is necessary to fit correctly this second Ge coordination sphere. The third-neighbour shell, around 4.6 Å, is constituted by Ge...Se interactions as for (c)GeSe₂. On the other hand, for DDF_{Se} (figure 5-b) Se is twofold coordinated and presents a mixed first-neighbour shell with Se-Ge ($N=1.3$, $R=2.36\text{Å}$) and Se-Se ($N=0.75$, $R=2.38\text{Å}$) bonds. The second intense peak is induced by Se...Se interactions, around 3.85 Å, while the third one is constituted by both Se...Ge and Se...Se

interactions near to 4.65\AA as for the (c)GeSe₂ structure.

-For (g)GeSe_s, an important structural change is noted, particularly for the Ge surroundings. For DDFGe, figure 6-a, germanium remains tetrahedrally linked with selenium ($N=4.4$, $R=2.36\text{\AA}$) but the Ge---Ge interactions corresponding to edge and corner sharing tetrahedra are not found. Thus, germanium is only surrounded by Se atoms located respectively around 3.7, 4.2 and 4.9 Å. For DDFSe, figure 6b, Se atoms present again a twofold mixed coordination with a more important part of homopolar Se-Se bonds ($N=1.45$) in this case. Furthermore, the Se---Se interactions near 3.42, 3.83 and 4.72 Å are rather similar to those encountered in the different structural forms of selenium. These results obtained for (g)GeSe_s seem to demonstrate that this structure is mainly constituted by isolated GeSe₄ tetrahedra in an amorphous Se matrix, in agreement with our 35K EXAFS results and with the "cross linked chains model" [11].

c) SAXS experiments:

All the SAXS spectra recorded for GeS_x ($1.5 \leq x \leq 7$) glasses are very similar. They present a monotonous decay of the scattering intensity $I(q)$ and have been fitted using a Debye Bueche model with correlation lengths of approximately 300 Å. These results show that GeS_x binary glasses present electron density inhomogeneities in a length scale inferior to 300 Å in accordance with the formation of different types of clusters in the glassy structure.

After improving our structural knowledge of the binary glasses (especially for (g)GeX₂), a structural study of ternary $(1-y)\text{GeX}_2 + y\text{Ag}_2\text{S}$ glasses has been undertaken.

3. TERNARY $(1-y)\text{GeX}_2 + y\text{Ag}_2\text{S}$ GLASSES :

This study has been mainly made on sulfide glasses because the glassy range is more extended for this system. We present here the EXAFS results characterizing the local surroundings of Ge, Ag and S atoms and the first SAXS experiments while an AWAXS investigation of these ternary glasses is in progress.

a) EXAFS results:

As for binary glasses, the three first Ge coordination spheres of ternary glasses have been investigated by Ge K-edge experiments made at 35K, figure 7. The structural parameters resulting from the analytical procedure [6] show an increase of GeS₄ tetrahedra distortion when Ag₂S is added to (g)GeS₂ in accordance with the room temperature results [8]. Furthermore, the Ag₂S addition seems to induce an important depolymerization of corner and edge sharing tetrahedra and an increase of M.R.O. structural distortion. Even if our data are of very good quality, we are at the technique's limit for second and the third shells of glass compositions containing more than 30% of silver sulfide ($y=0.3$), figure 7. These results can be related to the typical network modifier role played by Ag₂X, leading to the formation of Ag-S ionic bonds and the breaking of both double and single Ge-S-Ge bridges.

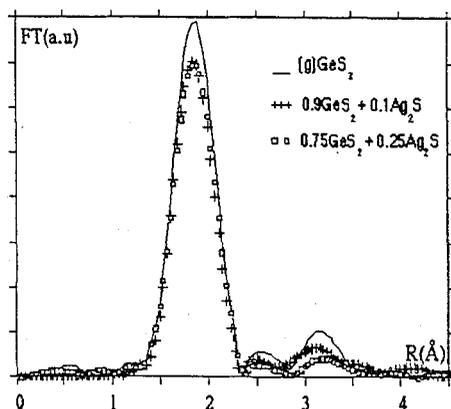


Figure 7: $k^3\chi(k)$ Fourier transform magnitudes at Ge EXAFS K-edge of (g) $(1-y)\text{GeS}_2 + y\text{Ag}_2\text{S}$ ($y=0.1$ and 0.25) compared to the (g)GeS₂ one.

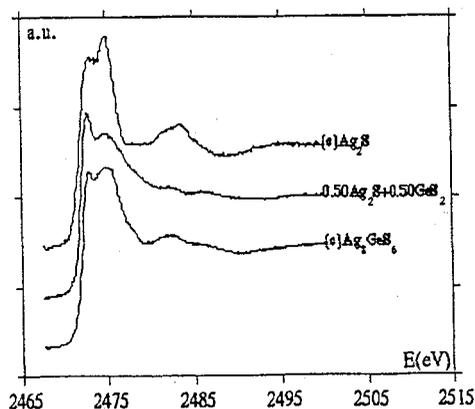


Figure 8: S K-edge XANES spectra of $\beta\text{Ag}_2\text{S}$, (c)Ag₈GeS₆ and (g)0.5GeS₂+0.5Ag₂S phases.

Due to the mobility of Ag^+ cations and to their distorted sites, only the first coordination sphere of silver has been characterized by room and low temperature Ag K-edge EXAFS study. At room temperature, each Ag atom is bonded to three sulfur atoms ($\text{Ag-S}=2.51\text{\AA}$) in very distorted sites. For weak Ag_2S proportions ($y < 0.3$), the silver sites in the glass seem close to those of $\beta\text{Ag}_2\text{S}$ [12] while for high Ag_2S contents ($y \geq 0.3$), the glassy silver sites appear close to those of (c) Ag_8GeS_6 [13]. These results are consistent with the low temperature EXAFS experiments [14] which show that the Ag thermal behaviour in the glasses ($y \geq 0.3$) is rather similar to the one of (c) Ag_8GeS_6 and different to that encountered in $\beta\text{Ag}_2\text{S}$ phase. Furthermore, the S K-edge XANES spectra confirm that the glasses with high Ag_2S content ($y \geq 0.3$) present sulfur surroundings more similar to those encountered in the Ag_8GeS_6 crystalline structure, figure 8.

These EXAFS results, obtained for ternary glasses, will be completed by AWAXS investigations already in progress.

b) SAXS experiments:

Unlike the binary glasses, the SAXS spectra of $(1-y)\text{GeS}_2+y\text{Ag}_2\text{S}$ glasses present an important evolution versus composition, (figure 9):

- For glasses with low Ag_2S concentration ($y=0.1$), the scattering intensity $I(q)$ shows a peak at $q=0.0169\text{\AA}^{-1}$ corresponding to a repetition distance of 370\AA obtained from the Bragg's law. Furthermore, the final part of $I(q)$ obeys Porod's law, $I(q)=f(q^{-4})$ [15], with a corresponding Porod radius, R_p , of 55\AA .

- When the Ag_2S proportion increases, the peak broadenes out to become a shoulder for $y=0.2-0.3$ glassy compositions and disappears for Ag_2S enriched glasses ($y \geq 0.3$), figure 9. On the other hand, the Porod region is made worse ($I(q)=f(q^{-3})$ for $y=0.2$ and $I(q)=f(q^{-2.5})$ for $y=0.3$) while the corresponding Porod radius is decreased significantly ($R_p = 20\text{\AA}$ for $y=0.2$ and $R_p = 17\text{\AA}$ for $y=0.3$). For $y \geq 0.3$ compositions, the scattering intensity, $I(q)$, presents weaker values and a monotonous decay which can be only simulated by a Debye Bueche model.

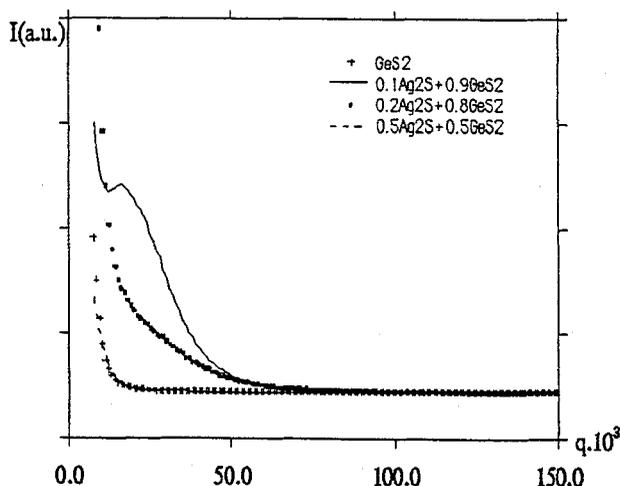


Figure 9: SAXS spectra of (g) GeS_2 and $(1-y)\text{GeS}_2+y\text{Ag}_2\text{S}$ ternary glasses.

These results seem to demonstrate that the glassy network modifier, for small amount of Ag_2S , is not well "dilute" in the glassy matrix. This induces the formation of Ag_2S clusters with sharp boundary for $y=0.1$ composition. The mean size of these clusters is about 55\AA in this case and their interaction distance is about 370\AA . When the Ag_2S percentage increases, the Ag_2S aggregates become smaller (20\AA for $y=0.2$) and there is no sharp boundary ($I(q)$ deviates from Porod's law). On the other hand, the Ag_2S cluster distribution in the glass is losing order as indicated by the broadening of the peak. This seems to demonstrate that the "dilution" of Ag_2S is improved, leading to a more homogeneous repartition of silver in the glass for Ag_2S enriched samples ($y > 0.3$).

This SAXS study, more macroscopic, is consistent with the results obtained for the local structure and would explain particularly the previous results registered for Ag K-edge EXAFS experiments. In order to

confirm these structural hypotheses, these first SAXS results will be completed by using the anomalous scattering effect (ASAXS).

4. STRUCTURAL CONCLUSIONS:

The EXAFS, AWAXS and SAXS analysis presented here are consistent among themselves and suggest for binary glasses that :

-All GeX_x binary glasses are chemically ordered and present a 4-2 coordinated network in agreement with the chemically ordered network model [5].

-The structures of glasses near GeX₂ stoichiometry are mainly based on that of the corresponding (c)GeX₂ network with the formation of layered clusters built up from GeX₄ tetrahedral units in agreement with the "outrigger raft" model [8,9].

-When the glassy composition deviates from GeX₂ stoichiometry, the homopolar bond proportion and the depolymerization of both corner and edge sharing tetrahedra increases significantly, in accordance with the lowering of glassy transition temperature T_g.

-For chalcogen enriched glasses, over GeX₄ composition, the glassy structure is essentially constituted by isolated GeX₄ tetrahedra in an amorphous chalcogen matrix in agreement with the "cross linked chains model" [11].

-The drastic structural evolution registered by AWAXS between GeSe₃ and GeSe₅ glasses agrees fairly well with the percolation/demixion threshold hypothesis around GeX₄ for these glasses.

For ternary glasses, the Ag₂S addition to the GeS₂ glass former gives rise to an important breaking of both double and single Ge-X-Ge bridges and to an increase of the structural distortions of S.R.O and M.R.O. This can be directly related to the typical network modifier role played by Ag₂X.

Nevertheless, for weak Ag₂X proportions, the structure of (1-y)GeX₂+yAg₂X glasses (0<y<0.3) could be demixed and constituted by two cluster types: layered clusters based on the (c)GeX₂ network and Ag₂X aggregates (≈50Å) based on the structure of βAg₂X. When the Ag₂X content increases, its "dilution" is improved leading to smaller clusters (≈20Å). For high Ag₂X contents (y≥0.3) the silver distribution would be more homogeneous in the glass leading to S.R.O. more similar to that of the Ag₈GeS₆ crystalline phase.

These structural hypotheses for ternary glasses resulting from EXAFS and SAXS experiments, will be completed by the characterization of the M.R.O. by an AWAXS study in progress, in order to better understand the Ag⁺ ionic transport process through the glassy structure.

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