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Glass forming tendency in Ga-Ge-S glasses: a structural approach

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Abstract:

We have studied by EXAFS glasses that belong to the $\text{Ga}_2\text{S}_3\text{-GeS}_2$ line around Ga and Ge K edges. Both tetrahedral GaS_4 and GeS_4 units are evidenced and low temperature measurements reveal ordering around germanium atoms up to 4 Å.

1. INTRODUCTION

Besides semiconducting chalcogenide glasses based on well known former elements as for instance germanium or arsenic, it exists a wide class of chalcogenide gallium based glasses which are not so often described. These glasses present a peculiar behaviour related to the impossibility to obtain bulk Ga-S or Ga-Se binary glasses by using conventional quenching. The glassy state is therefore reached by synthesis of more complex materials which contain either modifier elements (rare earth elements for instance) or some former elements (germanium for instance). These materials then support thermal and physical properties which are interesting for many applications (1-5). Some structural studies have been developed about these glasses (3) but they provided no explanation why binary sulfide gallium glasses do not exist and leave open the question of the low glass forming ability of gallium. One approach of this problem we present here is to study mixed gallium and germanium sulfide glasses in order to compare local and medium range order (if exists) around gallium and germanium atoms. We choose to work along the quasi-binary system $\text{Ga}_2\text{S}_3\text{-GeS}_2$ for which glasses are prepared in a wide extent on GeS_2 side. The structural technique we have used is the Extended-X-ray-Absorption-Fine-Structure well suited to investigate separately Ga and Ge surroundings.

2. EXPERIMENTS

All the bulk samples have been prepared from the $\text{Ga}_2\text{S}_3\text{-GeS}_2$ sulfides mixed according to convenient proportions. The mixtures were melt in silica ampoules at 1373K and then quenched in cold water. X-ray diffraction diagrams were registered to prove glassy state. We did thus prepare:

sample (1) 9 GeS_2 -0.5 Ga_2S_3

sample (2) 7 GeS_2 -1.5 Ga_2S_3

sample (3) 3 GeS_2 -1 Ga_2S_3

X-ray absorption spectroscopy measurements were carried out on the EXAFS II station at the DCI storage ring of LURE (Orsay) at the Ga(10367 eV) and Ge (11104 eV) K edges. We used transmission mode measurements at room temperature and 7 K by using a helium liquid cryostat. Energy selection was made using a Si (311) double crystal monochromator. Considering the relatively high energy of the K edges studied no rejection harmonic mirrors were used. The EXAFS analytical procedure has been fully described elsewhere (6) and we used single scattering theory and the plane-wave approximation with amplitudes and phases calculated by Mc Kale and al. (7). The σ^2 Debye-Waller factor and Γ whole state width were calibrated from crystalline reference compounds: αGeS_2 (quasi regular tetrahedral sulfide germanium with $R_{\text{Ge-S}}=2.22$ Å) and the $\text{La}_6\text{Ga}_2\text{Mn}_2\text{S}_{14}$ with a slightly distorted GaS_4 tetrahedral surrounding :

(3 $R_{Ga-S}=2.28 \text{ \AA}$ and 1 $R_{Ga-S}=2.23 \text{ \AA}$). The simple Ga_2S_3 binary compound presents a too wide distribution of Ga-S distances to be used as a reference. During the fitting procedures in the first steps we alternatively adjust N, R, ΔE , σ^2 parameters and at the final step all these parameters were authorized to vary. The Γ value when calibrated to the reference compound was let fixed.

3. RESULTS

The tables 1 and 2 give the fitting results about the Ga-S and Ge-S first shells coordination.

	N	$\sigma(\text{\AA})$	R($\text{\AA}$)
$La_6Ga_2Mn_2S_{14}$.	4	0.09	2.28
Sample 1	4.08	0.1	2.28
Sample 2	4.10	0.09	2.28
Sample 3	4.10	0.1	2.28

TABLE 1 : Fits results concerning the S shell around Ga atoms, in Ga_2S_3 - GeS_2 glasses at the room temperature.

	N1	$\sigma(\text{\AA})$	R1($\text{\AA}$)
αGeS_2 .	4	0.07	2.22
Sample 1	3.96	0.07	2.22
Sample 2	3.95	0.07	2.22
Sample 3	3.95	0.08	2.22

TABLE 2 : Fits results concerning the S shell around Ge atoms, in Ga_2S_3 - GeS_2 glasses at the room temperature.

For all these fittings the residue value was near 2.10^{-2} . We did not observe significant differences when we studied low temperature spectra except an expected decreasing σ^2 value. However these low temperature measurements revealed a second shell around the Ge atoms which is quite interesting and which permits to approach medium range order informations. The figure 1 shows the pseudo radial distribution function around the Ge K edge obtained by Fourier transform of the normalized signal EXAFS.

Fig 1 : FT moduli at the Ge K-edge, at 7 K.
* short Ge---Ge distance. (2.92 $\text{\AA}$)
** long Ge---Ge distance. (3.405 $\text{\AA}$)

In the range from 2.3 Å to 3.5 Å the second and third peaks observed in the glassy samples correspond to those observed in the crystalline αGeS_2 and of which origine is known. These peaks are due to two kinds of Ge---Ge interactions: a shorter distance (2.92 Å) related to edge sharing tetrahedra and a longer distance more complex with value of 3.405 Å related to corner sharing tetrahedra. This behaviour has been previously described by Armand and al.(8) relatively to the Ge-S glasses. Some attempts to fit these second and third shells on the crystalline reference compound (figure 2) and glass sample 2 (figure3) give the following results: (table3).

Fig 2 : Fit of the double peak corresponding to the short and long Ge---Ge distances in GeS_2 .

Fig 3 : Fit of the double peak corresponding to the short and long Ge---Ge distances in sample 2.

	N ₂	$\sigma(\text{\AA})$	R ₂ ($\text{\AA}$)	N ₃	$\sigma(\text{\AA})$	R ₃ ($\text{\AA}$)
αGeS_2 .	1	0.08	2.92	3	0.07	3.405
Sample 1	0.57	0.09	2.95	3.2	0.10	3.43
Sample 2	0.39	0.09	2.97	3.02	0.11	3.42

TABLE 3 : Fits results concerning the short and long Ge---Ge distances in Ga₂S₃-GeS₂ glasses.
(At the Ge K-edge and low temperature)

The more complex form of these peaks concerning the sample 3 with lowest concentration of germanium prevents us to fit this glassy composition. We conclude that in the Ga-Ge-S glasses, the germanium atoms keep the memory of the structural arrangement of the crystalline form αGeS_2 up to 4 $\text{\AA}$. When we compare the σ values related to the structural disorder which is the prevalent part concerning these very low temperature experiments we observe that this parameter is higher for the third shell than for the second one. That means that the corner sharing tetrahedra are more softly bounded than the edge sharing tetrahedra are, and that they are sensitive to addition of gallium atoms.

4. DISCUSSION

EXAFS Ga K edge analysis confirms the existence of strong GaS₄ units, but does not inform about the connection between these units. By analysing Ge K edge spectra we conclude to a tendency of clustering to GeS₄ units, some gallium atoms substituting germanium atoms inside the corner sharing tetrahedra and so distorting them. One question remains of the impossibility to evidence Ga---Ge interactions may be due to the quite identity of there backscattering amplitude functions. However we may advance that the GaS₄ tetrahedra do not form clusters and that may be an explanation of the impossibility to synthetize glassy Ga-S binary alloys.

Our results are not in agreement with models proposed by Ivanova (4) concerning the (GeS₂)_{100-x} Ga_x glasses studied by vibrational spectroscopy, neutron scattering and X-ray diffraction. These models do not respect GaS₄ tetrahedra which are well described by our EXAFS measurements and do not propose mixt edge and corner sharing GeS₄ tetrahedra.

Moreover our results bring structural informations which may be applied to the Ga-Ge-Se system , studied by Giridhar and al. (9), where selenium is in place of sulfur : in such glasses the gallium atoms probably present a four coordination and do not obey to the 8-N rule as we have observed in the Ga-Ge-S system here investigated.

REFERENCES

- (1) Loireau-Lozac'h A.M. ,Thèse d'Etat, Paris, (1977)
- (2) Auzel F., Michel J.C., Flahaut J.,Loireau-Lozac'h A.M., and Guittard M., *C. R. Acad. Sci. Paris* 291 (1980) 21-24.
- (3) Bénazeth S., Tuilier M.H., Loireau-Lozac'h A.M., Dexpert H., Lagarde P., and Flahaut J., *J. Non-Cryst. Solids* 110 (1989) 89-100.
- (4) Ivanova Z.G., *J. Molecular Structure* 245 (1991) 335-340.
- (5) Chbani N., Cai X., Loireau-Lozac'h A.M. and Guittard M., *Mat. Res. Bull.* 27 (1992) 1355-1361.
- (6) TEO B.K.,Basic principles and data analysis (Springerverlag, New York, 1986).
- (7) Mc Kale A.G., Veal B.W., Paulikas A.P., Chan S.K., and Knapp S., *J. Am. Chem. Soc.*, 110 (1988) 3763.
- (8) Armand P., Ibanez A., Dexpert H. and Philippot E., *J. Non-Cryst. Solids* 139 (1992) 137-145.
- (9) Giridhar A. and Mahadevan S., *J. Non-Cryst. Solids* 126 (1990) 161-169.