

## EXTENDED X-RAY ABSORPTION FINE STRUCTURE STUDY ON Bi MODIFIED GeS BULK GLASSES

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EXAFS measurements have been performed from the Ge K edge and Bi L<sub>III</sub> edge on GeS<sub>2</sub>Bi glasses with 6, 8 and 16 Bi at. %, and on crystalline Bi<sub>2</sub>S<sub>3</sub>. As expected, Ge is found to be fourfold coordinated with S atoms. It is also found that Bi is only coordinated with S with a coordination number CN = 4. This result for the CN of Bi contradicts the conclusion of Elliot and Steel. On the basis of the obtained CN of Bi, it is possible to exclude the presence of Bi<sub>2</sub>S<sub>3</sub> microcrystalline inclusions and to assert that these glasses are homogeneous at the microscopic level.

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### 1. Introduction

The first paper that dealt with the addition of bismuth in a chalcogenide matrix was published by Bowman and Schottmiller [1] in 1968. The goal was the preparation of new infrared photodetectors. At the same time, it was discovered that small amount of Bi atoms incorporated in a selenium matrix changes the electrical conductivity from p to n type [2]. More recently, the possibility of making an all chalcogenide glass p-n junction based on the ability of Bi to change the conductivity type was demonstrated [3,4]. Since the Schottmiller and co-workers results, many studies were performed to propose an explanation for the origin of this specific property that Bi atom seems to possess. Different atomic configurations were proposed. Most of these works were recently discussed in a synthesis paper of Vautier [5]. In regard to this last paper, one of the conclusions was that after more than 30 years of researches and debates, the origins of this specific property are not yet completely elucidated. In fact, one of the main problems is the lack of direct structural investigations of atomic Bi surrounding. Indeed, except the EXAFS works of Elliot et al [6] performed on GeS<sub>2</sub>Bi and GeSeBi glasses at the Bi absorption edge, to our knowledge no further direct investigations of the local surrounding of Bi atoms incorporated in a chalcogenide matrix were proposed.

In this work, structural results obtained on a series GeS<sub>2</sub>Bi glassy materials by means of EXAFS experiments are presented. The Ge and Bi absorption edges are explored.

### 2. Experiments and fitting procedure

Glasses were synthesised by direct melting of the ad-hoc amounts of high purity elements in vacuum sealed ( $10^{-3}$  Pa) silica ampoules at 900°C for 72 hours with continuous agitation. Glasses were obtained by quenching the tube in cold ice-water mixture.

EXAFS measurements in the transmission mode were performed at the Ge K edge (11103 eV) and Bi L<sub>III</sub> edge (13440eV), at the EXAFS III station using the beam delivered from the bending magnet at DCI in LURE (Orsay France). The Si 311 monochromator was used to select the beam energies for Ge K and Bi L<sub>III</sub> edge experiments. Experiments were performed at room temperature. Data were collected with an energy step of 2eV and 3eV for respectively Ge k and Bi L<sub>III</sub> edges, using ionization chambers as detectors. Three spectra were obtained for each sample. The samples

used in absorption measurements were prepared by crushing and grinding the materials into particles finer than 20  $\mu\text{m}$ , which were homogeneously pressed on kapton tapes.

The EXAFS spectra analyses were performed through a chain of programs written by Michalowicz [7]. The normalised EXAFS oscillations  $X(k)$  were obtained with the Lengeler-Eisenberger formula [8] with a linear model for the pre edge background removal and a five degree polynomial function to reproduce the post edge absorption. The EXAFS oscillations are approximately described by the following formula:

$$X(k) = \sum_j \frac{F_j(2k)N_j}{kr_j^2} \cdot \exp\left(\frac{-\Gamma_j r_j}{k}\right) \cdot \exp(-2\sigma_j^2 k^2) \cdot \sin(2kr_j + \Psi_j(k)) \quad (1)$$

$F_j(2k)$  is the backscattering amplitude from each  $N_j$  neighbouring atoms of the  $j^{\text{th}}$  type located at a distance  $r_j$  from the photoexcited atom (here Ge and Bi) and  $\Psi_j(k)$  is the total phase shift experienced by the photoelectron. Both  $F_j(2k)$  and  $\Psi_j(k)$  are chemically sensitive,  $\sigma_j$  is the Debye-Waller factor that is the standard deviation in interatomic distances relative to their mean value  $r_j$ . The damping factor  $\exp(-\Gamma_j r / k)$  is due to inelastic losses in the scattering process where  $\Gamma_j$  is related to the mean free path of the photoelectron.

Through the EXAFS analysis, the information about  $N_j$ ,  $r_j$ , and  $\sigma_j$  around the photoexcited atom can in principle be obtained for each coordination shell. The modulus of the sine Fourier Transform (FT) of equation 1 gives a pseudo radial distribution function (RDF) in real space. In our data treatment, the Kaiser window function is used, which is defined by  $\tau = 2.5$  in the range 3.5 eV to 12 eV. The FT of the  $k^2$  weighted EXAFS spectra were obtained. For these ternary chalcogenide based alloys, ab-initio calculations cannot be performed because of the lack of a reference material. Thus to simulate the EXAFS oscillations, we used theoretical phase and amplitude functions from Mac Cale et al. [9] which introduce a correction term  $\Delta E$  for the absorption edge.

### 3. Results

The Fourier transform of the experimental EXAFS signal obtained at the Ge K edge exhibits, for the entire studied samples, the same shape. Basically, as exemplified by Fig. 1, only one oscillation is observed. Fig. 2 shows as an example the experimental and the calculated filtered EXAFS signals obtained on  $\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$  at the Ge K edge. The comparison of these two curves, show that the experimental data are well fitted by the set of parameters given in Table 1. The same conclusions are obtained if comparisons are performed on the Fourier Transformed  $k^2$  weighted EXAFS spectra. The same procedure performed on  $\text{Ge}_{26}\text{S}_{68}\text{Bi}_6$  leads to the same remarks and the set of parameters are also given in Table 1.

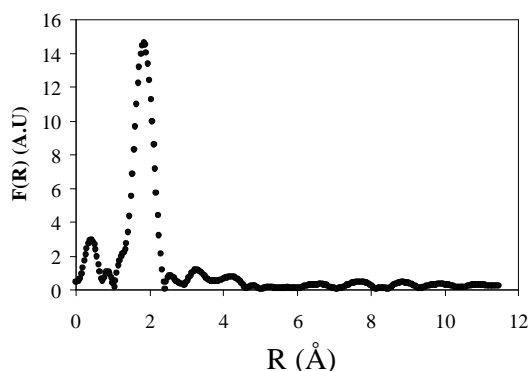


Fig. 1. Experimental Fourier transform of the EXAFS signal obtained at the K edge for  $\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$ .

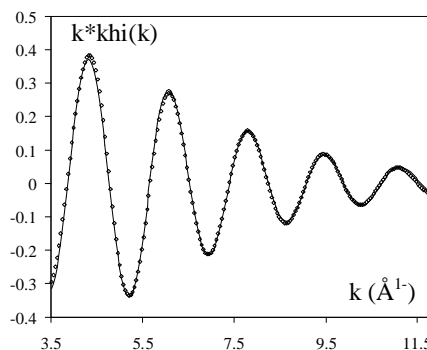


Fig. 2. Experimental (points) and calculated (line) of the filtered EXAFS signal obtained at the Ge K edge for  $\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$ .

Table 1. Results obtained after the fitting procedure given the surrounding of Ge atoms.  $\chi^2$  is the quality factor.

Material	N	r	$\sigma$	$\Gamma$	$\Delta E$	$\chi^2$
$\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$	4	2.24	0.066	0.43	10.4	$7 \times 10^{-4}$
$\text{Ge}_{26}\text{S}_{68}\text{Bi}_6$	4	2.24	0.076	0.51	9.8	$5 \times 10^{-4}$

Fig. 3 shows the experimental EXAFS signal obtained at the Bi LIII edge for all the studied samples. From these signals the filtered EXAFS signals corresponding to the first shell are obtained and simulated. The experimental data and the results obtained from the fitting procedures are displayed on Fig. 4. The sets of parameters obtained are given in Table 2. We may notice at this stage of the data presentation, that in any case the parameters used to fit the  $\text{Bi}_2\text{S}_3$  crystalline structure are able to fit the data corresponding to the ternary glassy alloys.

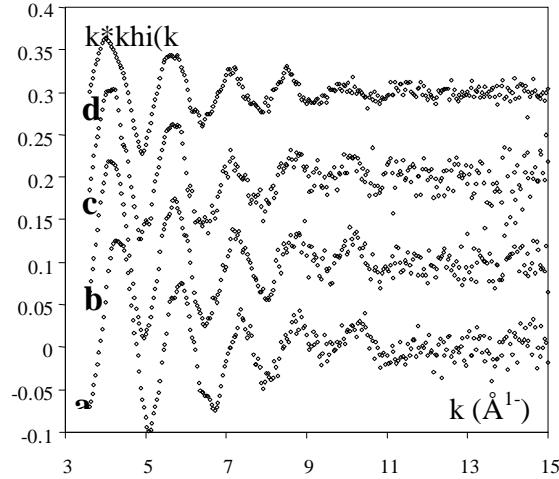
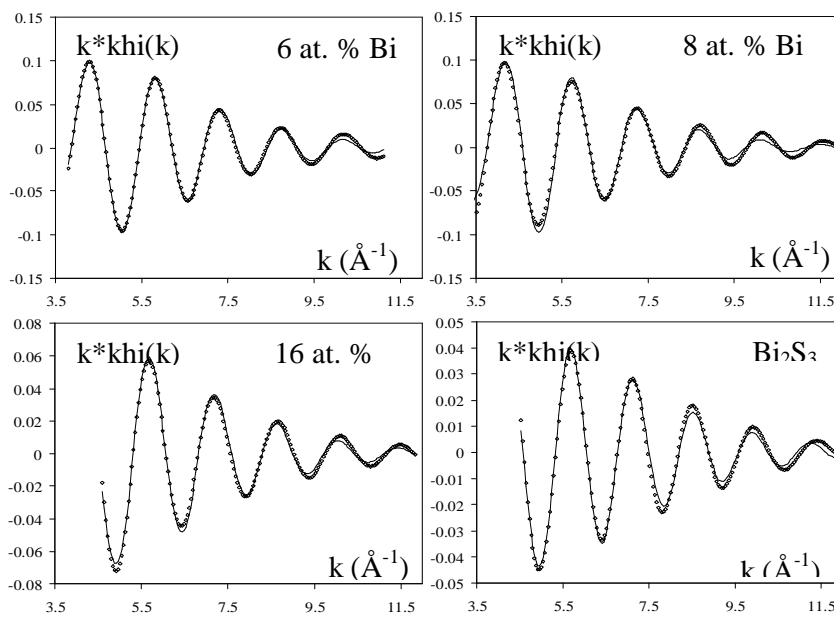

 Fig. 3. Experimental EXAFS signal obtained at the Bi LIII edge for glasses a)  $\text{Ge}_{26}\text{S}_{68}\text{Bi}_6$ , b)  $\text{Ge}_{26.7}\text{S}_{65.3}\text{Bi}_8$ , c)  $\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$  and for crystal d)  $\text{Bi}_2\text{S}_3$ .


Fig. 4. Experimental (points) and calculated (line) of the filtered EXAFS signal obtained at the Bi LIII edge for all the studied samples.

Table 2. Results obtained after the fitting procedure given the surrounding of Bi atoms.  
Results for  $\text{Ge}_{20}\text{S}_{77}\text{Bi}_3$  and  $\text{Ge}_{20}\text{S}_{70}\text{Bi}_{10}$  come from ref. 6.

Material	N	r	$\sigma$	$\Gamma$	$\Delta E$	$\chi^2$
$\text{Bi}_2\text{S}_3$	3.02	2.65	0.10	1.4	6.25	$2.2 \times 10^{-5}$
$\text{Ge}_{26}\text{S}_{68}\text{Bi}_6$	3.90	2.59	0.10	0.92	5.1	$6.3 \times 10^{-5}$
$\text{Ge}_{26.7}\text{S}_{65.3}\text{Bi}_8$	3.85	2.60	0.11	0.87	3.2	$2.5 \times 10^{-4}$
$\text{Ge}_{20}\text{S}_{64}\text{Bi}_{16}$	4.02	2.60	0.11	1.28	1.97	$3.2 \times 10^{-5}$
$\text{Ge}_{20}\text{S}_{77}\text{Bi}_3$	$3 \pm 0.5$	2.54	0.06			
$\text{Ge}_{20}\text{S}_{70}\text{Bi}_{10}$	$3 \pm 0.5$	2.56	0.08			

#### 4. Discussion

From data reported in Table 1, we observed that Ge atoms are fourfold coordinated with S atoms located at 2.24 Å. No homopolar Ge-Ge or heteropolar Ge-Bi bonds exist in these glassy ternary alloys. This result is not surprising and is basically found for all the Ge-chalcogenide alloys as GeSe [10,11] and GeTe [12,13], as far as the Ge content remains low enough. Thus as in most cases the local surrounding of Ge atoms in chalcogenide based alloys leads to the formation of  $\text{GeX}_4$  tetrahedral units (X being the considered chalcogenide atoms).

From data reported in Table 2, Bi atoms are also found fourfold coordinated with S atoms located at 2.60 Å. this coordination number for Bi atoms is found for both low and high Bi content. Moreover, the values of the other parameters resulting from the fitting procedure i.e. the Debye-Waller factor, the  $\Gamma$  factor are also found very similar. In Table 2 the results obtained by Elliot et al. [6] on other compositions are presented. These authors have found that the coordination number of Bi was  $3 \pm 0.5$  with a first coordination shell located at  $\approx 2.55 \pm 0.02$  Å for 3 at. % and 10 at. % Bi. Differences occur between these two compositions only on the Debye-Waller factor values, which is twice when composition passes from 3 at. % to 10 at. % Bi. We believe that this discrepancy between these two sets of experimental results could come from two different ways. The first concerns the sample preparation. Indeed, as previously mentioned on other glassy chalcogenide alloys [14-16], small differences in: the values of the upper temperature used for melting operation; the maintenance times at this temperature; the value of the cooling rate (never well known); can lead to important differences in the local order of the resulting glass. Basically, this problem is insoluble. The second concerns the fitting procedure. Indeed, as we have well observed on the GeSeIn system [17,18], different sets of N, r,  $\sigma$ ,  $\Gamma$  values can lead to the same apparent good fit of experimental data. This point is rarely mentioned in the literature but is often the source of many problems. To carry out the data fitting procedure, we have performed the following steps:

- i) The number of nearest neighbours N is fixed in such a way that the amplitude of the experimental signal is approximately fitted.
- ii) The radius r of the first coordination shell is also fixed.
- iii)  $\Delta E$  is the first quantity allowed to vary
- iv) r is the second quantity allowed to vary then both  $\Delta E$  and r vary simultaneously.
- v)  $\sigma$  varies, then  $\sigma$ ,  $\Delta E$  and r vary simultaneously.
- vi)  $\Gamma$  varies, then  $\Gamma$ ,  $\sigma$ ,  $\Delta E$  and r vary simultaneously.
- vii) Finally N is allowed to vary, then all quantity vary simultaneously.

The last step is repeated until the quality factor ( $\chi^2$ ) reaches a constant minimum value. We have to say, that with this fitting procedure, the EXAFS signal cannot be fitted with  $N = 3$  or  $N = 3.5$ .

On the other hand, as observed by Elliot et al [6], we find that there is no similarity between the EXAFS spectra for Bi doped glasses and the crystalline structure ( $\text{Bi}_2\text{S}_3$ ). Thus in agreement with Elliot et al. and at the difference of other ternary chalcogenide systems as GeTeSb [12,13], or GeSeIn [17,18], any significant proportions of microcrystalline regions (clusters or micro clusters) are found. With other words, Bi atoms are well dissolved and from an homogeneous way in the chalcogenide matrix.

## 5. Conclusion

As a conclusion we may propose the structure presented on Fig. 5 for GeS<sub>2</sub>Bi glassy alloys. The latter may be resumed as follow. Ge atoms are covalently bonded to four S atoms forming tetrahedra units. In regards to the studied composition most tetrahedra must be connected together by common S atoms leading to a tetrahedra formed network. Bi atoms are connected to four tetrahedra by making bonds with S atoms. One consequence is that the disorder supposed to be produced by the introduction of Bi atoms does not concern short-range order or medium or long range order but modification of the GeTe<sub>4</sub> tetrahedra network.

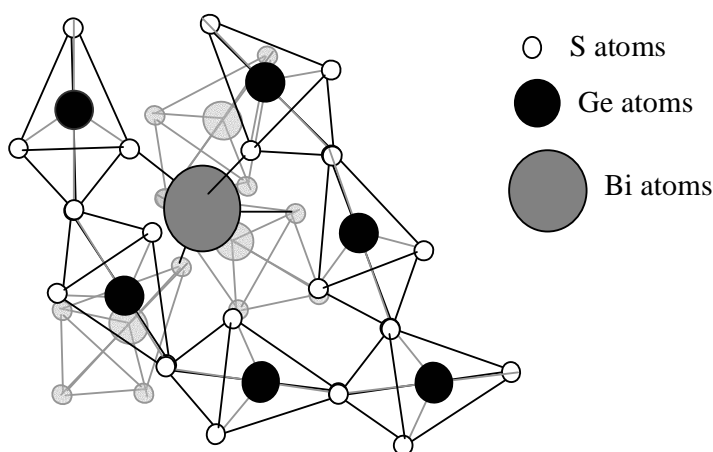


Fig. 5. Structural model proposed for Ge S Bi glassy alloys.

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