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ATOMIC SCALE STRUCTURE OF $Ge_{30}As_4S_{66}$

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The structure of a glassy sample of $Ge_{30}As_4S_{66}$ has been measured by means of synchrotron radiation. X - ray diffraction data were processed and the atomo-electronic radial function (AERDF) was calculated. The high resolution AERDF curve allowed for an accurate determination of the first order distances between the atoms and the coordination numbers. A model of spatial structure, based on the concept of raft configuration was tested. An other model of the structure based on the continuous random network concept (CRN) was tried. The general conclusion drawn from this study supports the idea that raft and disordered configurations interlinked so that the dangling bonds in the structure be minimized, is the best model for such type of glass.

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1. Introduction

The chalcogenide glasses are based on the combinations of chalcogens (sulphur, selenium, tellurium) with other elements. Binary, ternary and more complex glasses have been prepared and investigated up today [1-10]. The interest in these glasses stems from their particular properties related to the interaction with light and their applications in the information storage devices, holography, serography and numerous other fields of microelectronics and optoelectronics [11-15].

In spite of the great amount of studies, the structure of the chalcogenide glasses is not completely understood. There are many models for the structure of various type of simple and complex glasses [16-20]. One of the most intriguing glass is that one based on the combination of germanium with sulphur or selenium.

In order to explain the structure of such glass and especially the companion A1 Raman peak line, Bridenbaugh et al. [21] assumed a model according to wich glassy $Ge(S,Se)_2$, in sharp contradistinction to glassy SiO_2, does not consist of a random (i.e. fully three- dimensional) network [22]. Instead the covalent network glassy $Ge(S,Se)_2$ is made up of stacked chalcogenide-covered wafers, with an average diameter and stacking thickness of order 10 ÷ 20 Å. The clusters proposed for the glass structure are known as “outrigger rafts”. They are composed of stacked rafts. The model was extended to glassy As_2S_3 to yield orpimental rafts.

We have investigated the structure of a GeS_2 based glass with low amount of arsenic: $Ge_{30}As_4S_{66}$. High resolution X-ray diffraction patterns obtained with synchrotron radiation allowed for getting accurate structural data. The experimental data were compared to the data resulted from the computer – assisted modelling of the glass in two cases: a model with outrigger rafts and a continuous random network model.

2. Experimental

To get a glassy $Ge_{30}As_4S_{66}$ sample, elemental Ge (99,999%), As (99,999%), S (99,999%) in correct ratios were sealed in quartz ampoule after cleaning and outgasing it by heating to 900 ˚C in

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vacuum. The filled ampoules were vacuumated at 1×10^3 Pa for 30 minutes. The content was thoroughly mixed in a rocking furnace at 650 °C for 24 hours before being quenched in water.

The X-ray diffraction measurements have been carried out in the experimental station of synchrotron radiation BW5, HASYLAB, Hamburg, Germany. The powdered sample has been introduced in a quartz capillary of 2 mm in diameter with walls of 0.02 mm. The energy of the X-ray radiation was 123.5 keV (λ = 0.1 Å). The thickness of the beam was 1×4 mm^2 and the scattered X-ray radiation has been measured in the range 0.5 – 20 Å^{-1}. Corrections of air scattering, polarization, absorption and error in the solid angle of the detector have been performed.

The X-ray diffracted intensity was processed in order to get the atomo-electronic radial distribution function of the material.

3. X- ray diffraction results

Figure 1 shows the X-ray reduced intensity, i(s) ($s=2\sin\theta/\lambda$), of the glassy $Ge_{30}As_4S_{66}$ sample. The first sharp diffraction peak is well expressed at s = 0.1633 Å^{-1}. This position corresponds to the quasi-distance of 6.124 Å and an inter-layer spacing of 7.532 Å (according to the relation $d_{interlayer} = 1.23\times d_{FSDP}$).

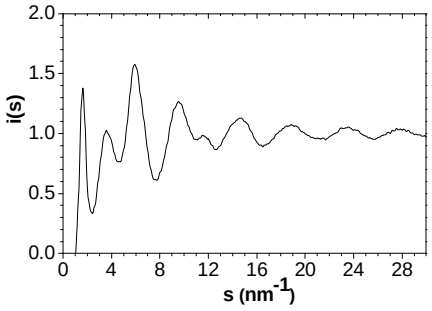

Fig. 1. The X-ray diffraction diagram of the glassy $Ge_{30}As_4S_{66}$ sample.

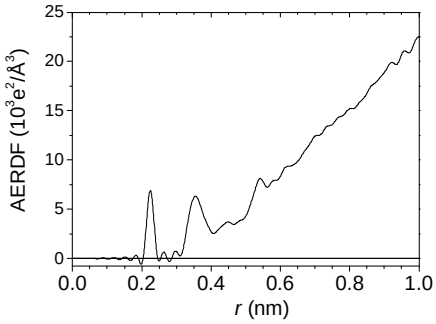

Fig. 2 The radial distribution function of the glassy $Ge_{30}As_4S_{66}$ sample.

The atomo-electronic radial distribution function (AERDF) of the sample is shown in figure 2. The first peak in AERDF is situated at 2.246 Å. This distance corresponds to the sum of covalent radius of germanium and sulfur: 1.225 Å+1.035 Å = 2.250 Å. The second peak in AERDF is situated at 3.54 Å. The large width of this peak (0.6 Å) speaks in favour of a large distribution of the bond angles, wich is correlated to a large disorder in the glass.

4. Modelling

Two models have been developed for the $Ge_{30}As_4S_{66}$ glass. First, the raft model of GeS_2 glass has been constructed according to the proposal of Bridenbaugh et al. [21]. These author proposed the outrigger raft model for the GeS_2 glass and drawn a possible raft structure able to explain the Raman data. The outrigger raft model contains 58 simulated atoms, connected as shown in figure 3.a, based on schema from the paper [21]. The composition is $Ge_{18}S_{40}$, but taking into account the borders of te cluster with unsatisfied bonds the true composition, considering the marginal atoms in right proportion becomes: $Ge_{17}S_{34}$. Bridenbaugh et al. considered, for the sake of simplicity in the calculation of the structure, direct bonds between the marginal sulfur atoms with dangling bonds. We calculated their model with direct S-S bonds. Additionaly, we calculated a model whith 6 arsenic atoms introduced between sulfur atoms (Fig. 3b). The composition of the new

outrigger raft $Ge_{18}As_6S_{40}$. Taking into account the marginal atoms we have the true composition: $Ge_{17}As_4S_{40}$, that approaches more the glass composition investigated in this paper.

Both outrigger raft models have been relaxed by a Monte Carlo – Metropolis computer assisted procedure. In order to create a spatial outrigger raft model we have superposed five relaxed outrigger rafts at a van der Waals distance and with different orientation of every raft. The superposed rafts were rotated with not-correlated angles, in order to get a disordered packing in the structure. The superposition of the rafts were made at a distance of 7.532 Å, which corresponds to the interlayer distance estimated from the first sharp diffraction peak of the glassy sample.

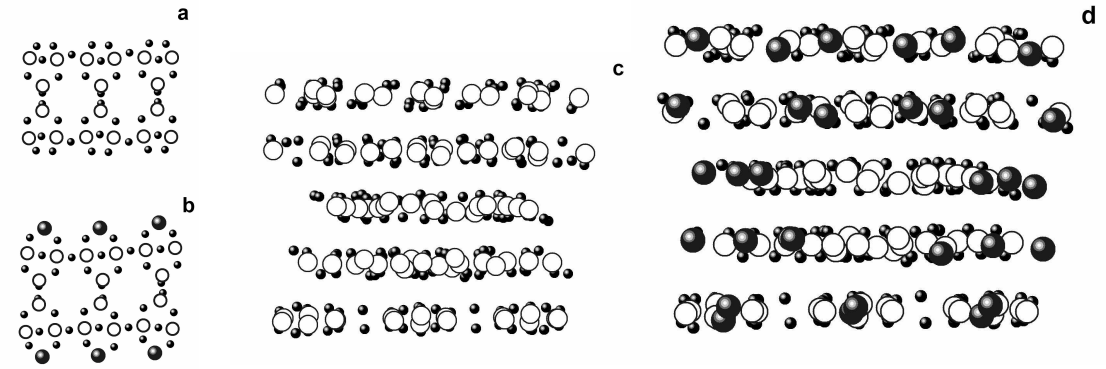

Fig. 3. The outrigger raft configuration and the model with superposed rafts. ● - As; ○ - Ge; ◕ - S
a. GeS_2 outrigger raft model b. $Ge_{18}As_6S_{40}$ outrigger raft model
c. Superposition of 5 simple rafts $Ge_{18}S_{40}$ (rotated by 65°,100°,150° and 165° relative to the central raft); inter-raft distance: 7.532 Å
d. Superposition of 5 simple rafts $Ge_{18}As_6S_{40}$ (rotated by 65°,100°,150° and 165° relative to the central raft); inter-raft distance: 7.532 Å

The second model is a continuous random network model with 124 atoms. Firstly, a model approaching GeS_2 was devised. The atomic composition is $Ge_{45}S_{79}$, but due to the dangling bonds of germanium, the formula GeS_2 is more appropriate in describing the structure. No homopolar bonds were allowed into the model. In the second stage, As atoms were introduced on the positions of those sulfur atoms that approches strongly one to another. Thus a new Ge – As – S random model was obtained. The relaxation of the models has been made in the frame of valence force field theory with the Keating-type potentials [23].

A Monte Carlo method for reaching the minimum free energy of the model was applied. The results of modelling for the two random models are shown in figures 4 and 5.

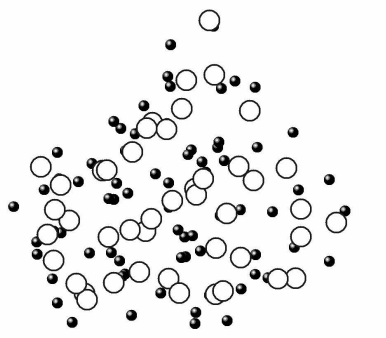

Fig 4. Continuous random network model of $Ge_{45}S_{79}$

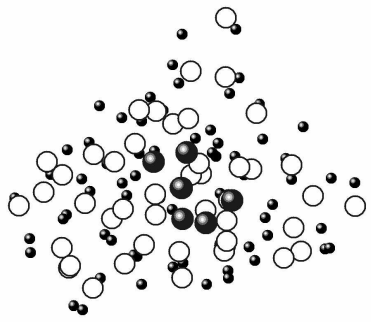

Fig.5 Continuous random network model of $Ge_{46}As_6S_{72}$

● - As; ○ - Ge; ◕ - S

5. Results of modelling

The relaxed outrigger raft model has been processed in order to get the bond angle distributions, the atom-pair distributions and structure factors. The characteristics of the outrigger raft model of GeS_2 with and without arsenic, as well as those of the random models are shown in figure 6.

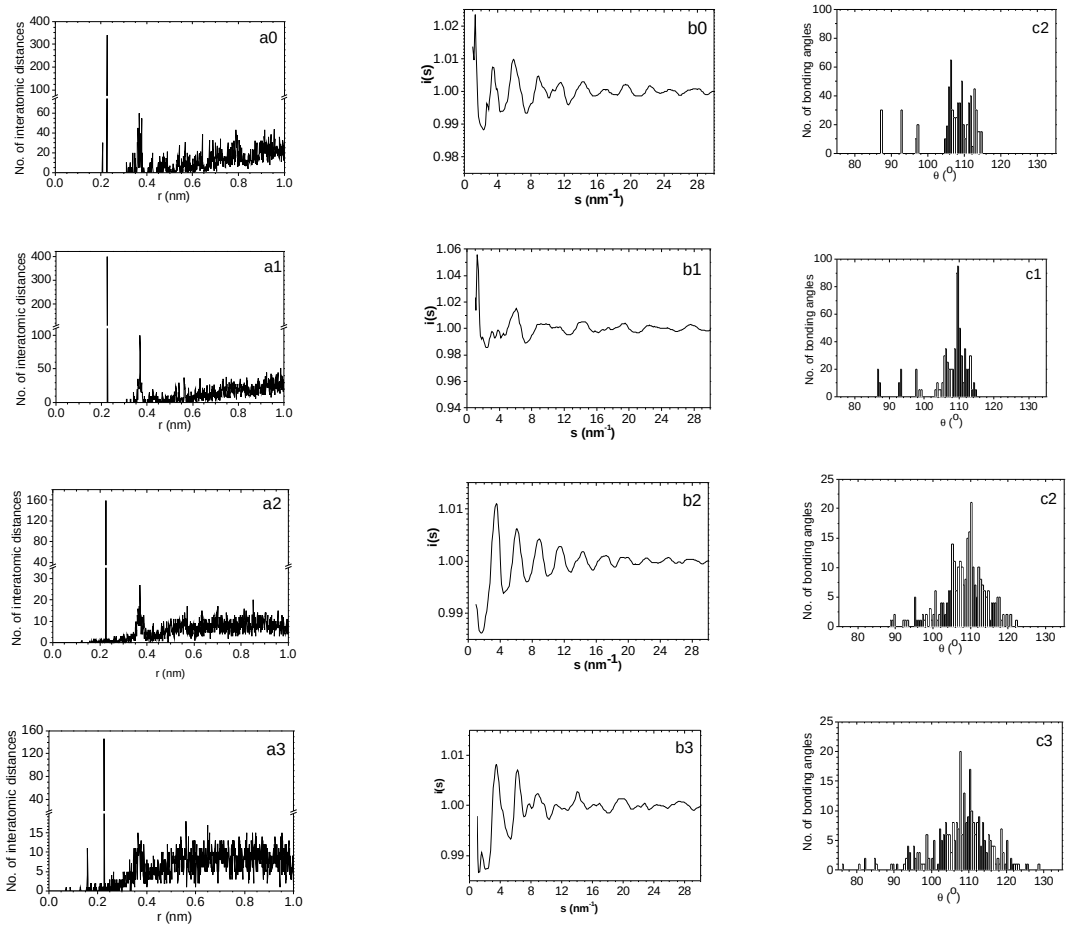

Fig. 6. Structural characteristics of the :
(0) spatial outrigger raft model $Ge_{18}S_{40}$ (interraft distance: 7.532 Å) (rafts rotated by 65°,100°,150° and 165° relative to the central raft)
(1) spatial outrigger raft model $Ge_{18}As_6S_{40}$ (interraft distance: 7.532 Å) (rafts rotated by 65°, 100°, 150° and 165° relative to the central raft)
(2) Continuous random network model of $Ge_{45}S_{79}$
(3) Continuous random network model of $Ge_{46}As_6S_{72}$
a. atom pair distance distribution; b. structure factor; c. bond angle distribution.

The main characteristic of the raft model is the presence of the first sharp diffraction peak in the structure factor. The peak is narrow and shows high intensity (Fig. 6-b2). Its position agrees with that evidenced on the experimental X-ray diffraction curve. The pair distribution function show peaks in the position of the first and second order neighbours. The second peak is much larger than the first one. The width of the second peak is 0.4 Å, a value different from that got from the experimental radial distribution function: 0.6 Å (Fig. 2). In the pair distribution function of the continuous random network model (Fig. 6a3) the width of the second neighbour peak is ~0.7 Å a value that overcomes the experimental value.

The modelling results show that the probably structure of the glass is given by linking more disordered regions and less disordered regions (outrigger raft-type). The calculation of the density in both models shows that the glass density is lower in the outrigger raft model and higher in the continuous random network model. The experimental value (2.8 g/cm^3 [24]) is situated in between the densities of the models developed for the glass sample.

An other observation is related to the first peak (situated after FSDP) in the structure factor of the models and glass. This peak is underdeveloped in the raft model, while in the CRN model is strong (more expressed than in the experimental curve (Fig. 1). Again, a combined outrigger raft +CRN model is able to account for the structure of the glass under study.

Recently we have proposed new configurations for the structure of chalcogenide glasses: nanotube configurations and various closed clusters [25,26]. These configuration could be a useful ingredient not only in arsenic chalcogenide but also in germanium chalcogenide glasses.

6. Conclusions

The structure of a glass based on GeS_2 with 4 at.% As has been determined. The X- ray diffraction data coupled with the modelling investigations have demonstrated that the most probable structure is given by a not homogenous network with regions expressing a quasi-layer type stacking interlinked with regions of random network, where the amount of homopolar bonds is kept minimum.

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