

## CLUSTER MODEL OF $\text{As}_2\text{S}_3$ GLASS

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Various closed nano-cluster configurations based on the stoichiometric arsenic-chalcogen composition have been used in the construction of the glass network of  $\text{As}_2\text{S}_3$ . A model with random packing of various large, closed nano-clusters, gives a good agreement with the experimental diffraction data for  $\text{As}_2\text{S}_3$ .

### 1. Introduction

De Neufville, Moss and Ovshinsky [1] were the first who suggested that a freshly evaporated film of  $\text{As}_2\text{S}_3$  was in fact a molecular glass composed of “hard sphere”  $\text{As}_4\text{S}_6$  molecules. When heated or illuminated, the film polymerize or cross-link to form a network structure characteristic of bulk glass. Weiqing Zhou, Paesler and Sayers [2] have shown by X-ray absorption fine structure measurements that films prepared by flash evaporation from  $\text{As}_4\text{S}_4$  source material have, as a basic component the cage like  $\text{As}_4\text{S}_4$  molecule. The molecules are disorderly packed as compared to those of crystalline  $\text{As}_4\text{S}_4$  (realgar).

Apling, Leadbetter and Wright [3] have simulated a molecular glass having as a basic building unit the  $\text{As}_4\text{S}_6$  molecule. The simplest model is described by a random sphere packing that assumes an effective molecular diameter of 0.64 nm and a packing fraction of 0.532. The model gives an excellent fit to FSDP but there are obvious deficiencies in the middle range of the scattering vector. The sharpness of the FSDP in the model is easily adjusted by varying the packing fraction and altering the effective molecular diameter to maintain the overall density roughly measured on a film of  $\text{As}_2\text{S}_3$ .

The aims of this paper is to present a structural model for  $\text{As}_2\text{S}_3$  built from closed clusters, and to compare with the experimental structural data (X-ray diffraction and radial distribution function).

### 2. Modelling

At first, cage-like clusters of different size, and planar-like clusters with closed ends and without dangling bonds, were physically built from special plastic units. These clusters are based on arsenic and chalcogen atoms in stoichiometric proportions. Every unit simulates a sulfur atom with two bonding directions, or an arsenic atom with three bonding directions.

The coordinates of the simulated atoms of the hand-built clusters have been measured directly on the 3D physical models. The coordinates and the first coordination sphere of every atom were tabulated and been used as input data in a dedicated program for the energy relaxation of the structure. The equilibrium distance between the As and S atoms was taken 0.225 nm, the bond angle on sulphur  $106^\circ$ , and the bond angle on arsenic  $98.7^\circ$ , as shown by Rubinstein and Taylor [4].

The structures of minimum free energy have been calculated by an iteration procedure based on Monte Carlo – Metropolis method by using the rule of minimization of the distortion energy (energy relaxation) for the whole model. The associated free energy of the model was calculated with the use of the force constants taken from literature. These are the bond stretching force constant and the bond bonding force constants for the angles between bonds formed by arsenic and sulphur atom. The bond stretching potential centered on As-S equilibrium distance,  $r_0$  was taken as

$V_1=A(r^2-r_0^2)^2$  with  $A=2.4\times 10^{-5}$  dyn/Å<sup>3</sup>. The bond bending potentials were centered on the sulphur equilibrium bond angle and on the arsenic equilibrium angle between bonds,  $\alpha_0$ , was taken as  $V_2=B(\alpha-\alpha_0)^2$  with  $B=2.04\times 10^{-4}$  dyn.Å/rad [5,6].

### 3. Model of amorphous As<sub>2</sub>S<sub>3</sub>

From the very beginning of the modelling, we propose a model, which is built up from only completely closed building units, and having only heteropolar bonds. At this stage of the modelling we do not allow any homopolar (“wrong”) bond, nor any other kind of defect.

The main contribution to the reproduction of the experimental RDF we suppose here to be given by the interplay between three kind of distances, defined by the followings: 1. the bond length; 2. the internal distances which appear implicitly in a building unit, between the constituent atoms of the unit; and 3. the packing distances from between the building units.

From theoretical point of view, modelling of these structures is very important, because the lack of experimental data which might be used to decide unambiguously about the reality of one or another structural configuration. So, even if the modelling might be rough at this stage, it might show if the basic idea brings us closer or not to the experimental results. Obviously, the model can be refined later on.

The above mentioned three kind of distances, and their distribution, is supposed to be strictly energetically controlled. As minimal constraint conditions which a model must fulfil to be considered realistic enough, are the following: 1. to not display interatomic distances shorter than a bond length; 2. to keep bond angle distribution in a realistic range, according to data from the literature for the given bond type, and 3. to reproduce as good as possible the experimental density.

Taking into account the possibility to build a wide range of closed clusters in the glassy composition, we have tried to develop a model for As<sub>2</sub>S<sub>3</sub> made by packing different type of clusters. We have packed large extended nano-pie clusters including small polymerized nano-pie ones. Cage-like clusters have been added. Two disordered As<sub>2</sub>S<sub>3</sub> layers (159 atoms in every layer) have been also included in the model. The final heap of clusters (Fig. 1a) has been investigated as concerning the structural properties. Firstly the structure factor (diffraction pattern) has been calculated (Fig. 1b). The most important characteristic is the strong development of the FSDP. The position and width of this peak agree satisfactorily with those obtained from experiment. The other diffraction peaks are situated in the right position. The radial distribution function is also in fairly good agreement with the experimental one (Fig. 1c). Of course the model is not perfect because we do not know the true ratio of different type of clusters in the glassy composition. A good model must have a correct density. The density of the model (2.85 g/cm<sup>3</sup>), is at variance with that experimentally found for bulk As<sub>2</sub>S<sub>3</sub> (3.195 +0.015 g/cm<sup>3</sup> [1]), and this feature could be explained by the voids that remain when clusters of various geometries are packed. Other explanation could be the finite size of the model, which influences the correct estimation of the density.

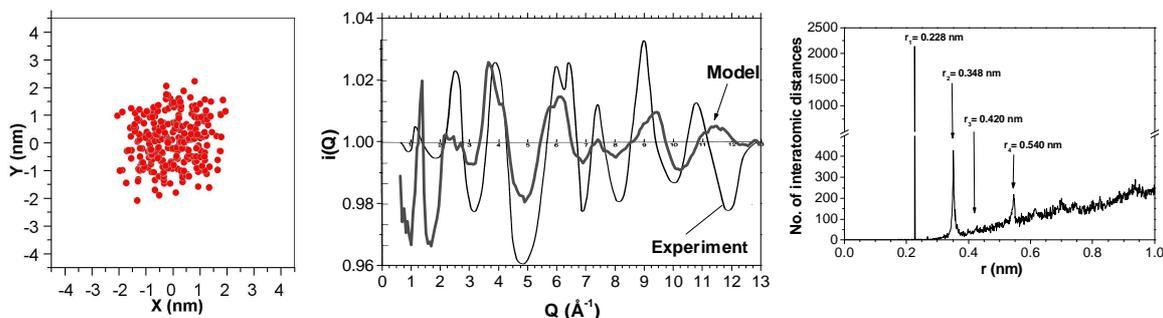


Fig. 1. a. a-As<sub>2</sub>S<sub>3</sub> model; (1799 atoms) b. Comparison of the reduced diffracted intensity curve calculated from the model (full curve) with the experimental curve (grey curve). c. Radial distribution function of the model; the arrows indicate the position of the peaks in the experimental RDF of As<sub>2</sub>S<sub>3</sub>

#### 4. Conclusions

Several types of closed nanoclusters of  $\text{As}_2\text{S}_3$  were built. A model of glassy  $\text{As}_2\text{S}_3$  was developed by packing such closed nanoclusters. The fairly good agreement of several characteristics, calculated from the model, with the experimental ones allows to conclude that a model with closed ends is very attractive and could be improved.

The new model of glassy chalcogenides with large closed clusters allows for a simple explanation of the photoinduced phenomena, taking into account the interaction between clusters at the boundaries, assisted by light. Moreover, a bistable behaviour of the clusters could explain the behaviour of the glass under the action of various external factors (radiation, pressure, temperature...)

An important feature of the model is the absence of the dangling bond-type defects, and the lack of a significant amount of valence alternation pairs (VAP) defects. The VAP amount is minimized because all the clusters are completely closed.

#### References

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