

MODELLING OF LARGE MOLECULAR CLUSTERS IN THE NON-CRYSTALLINE As_2S_3

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Modelling of several large molecular clusters possible to be formed in non-crystalline arsenic chalcogenides (As_2S_3 , As_2Se_3 or mixed compositions) during cooling down of the melts has been performed. The structure of minimum free energy was calculated in the frame of valence force field theory using a Monte-Carlo-Metropolis method. The structural characteristics of the clusters were computed after energy relaxation. There was demonstrated that specific cluster configurations of the type *nano-hat*, *nano-pie* and *nano-tube* are crystallo-chemically compatible with the non-crystalline structure of the arsenic chalcogenides.

The structure of the arsenic chalcogenides in the amorphous or glassy state is still challenging in spite of a huge effort dedicated to this problem and of interest related, in special, to the photostructural properties of these materials [1-18]. Recently, new applications of the chalcogenide glasses in Ovonic Cognitive Computer [19] based on Ovonic Phase Change Materials, in optical programmable metallization cell technologies [20], in optical recording [21], in optical fibers [22], in gas sensors [23], and in lift-off photolithography [24], renewed the top interest into these materials.

The typical representative of the large class of chalcogenides is As_2S_3 . This material is difficult to get in the crystalline state and is very stable in the glassy state. The large difference between the atomic scattering factors of arsenic and sulphur determines, on one hand, a high first sharp diffraction peak (FSDP) in the X-ray diffraction pattern and, on the other hand, gives more sensitivity of this pattern to the atomic scale arrangement in the material.

We have built from plastic units large clusters of As_2S_3 with the rules: (a) only As-S bonds are permitted, (b) no dangling bonds are permitted and (c) the number of 12 atoms per ring, specific to orpiment crystal (As_2S_3), is maximised in a every molecular cluster. In this paragraph communication we present two such clusters, and for the sake of comparison is added the third one, already, reported (the nano-tube) [25].

The first molecular cluster (Fig. 1 a1, b1) is the *nano-hat* cluster characterised by 7 rings with 12 atoms (6 As and 6 S), 6 rings with 6 members and a very large ring defined by 24 atoms, at the margin. The cluster contains 60 atoms (24 As and 36 S).

The second molecular cluster, the *nano-pie* cluster (Fig. 1 a2, b2) contains 180 atoms (72 As and 108 S). It exhibits a double layer configuration with 26 rings with 12 atoms, and 12 ten-fold rings.

The cluster represented in Fig. 1 a3, b3 is a *nano-tube* with open ends containing 34 rings with 12 members (194 atoms of which 68 As and 126 S). The coordinates of the atoms were carefully measured directly on the models. The tables of co-ordination were recorded. These data were introduced in computer and every structure was relaxed energetically in the frame of a Monte-Carlo-Metropolis procedure, using the force field theory [26] with appropriate force constants (bond stretching and bond bending force constants) [27]. The equilibrium parameters were chosen as the mean values of those from orpiment: the As-S bonding distance of 0.225 nm, and the bonding angle of 101° .

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The results are presented in Fig. 1. Two projections of every relaxed cluster are shown (a1-b1; a2-b2; a3-b3). The histograms of interatomic distances (pair distribution function – PDF), the bonding angle histograms, and the structure factors are presented in the sections c, d and e of Fig. 1.

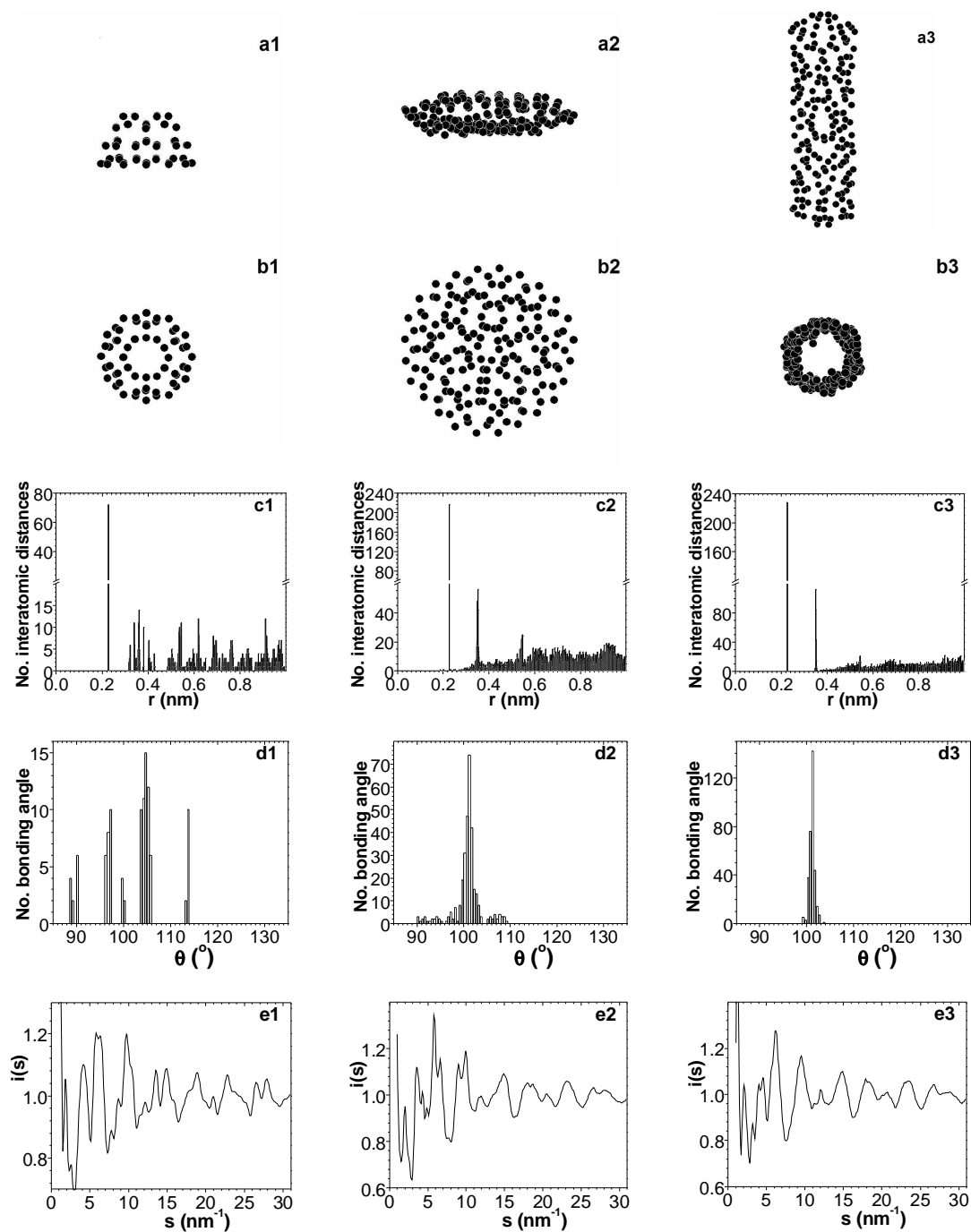


Fig. 1. Molecular clusters based on As_2S_3 ; 1. Nano-hat clusters, 2. Nano-pie cluster, 3. Nano-tube cluster; a, b. two projections of the atomic structure; c. pair distribution histograms; d. bond angles distribution, e. structure factors.

One surprising fact is the appearance of the FSDP in the diffraction pattern calculated for every model. Its position corresponds to that known from the experimental X-ray diffraction

patterns, carefully determined by Neufville, Moss and Ovshinsky [28], and Young and Thege [29]. This gives the hope to get a good structural model for As_2S_3 by packing together such molecular clusters. The nano-pie cluster is characterised by a narrow bond angle distribution, while the nano-hat has the bonding angles distributed into 5 angular groups. The nano-tube exhibits the narrowest angular distribution. The pair distribution histograms evidence a very broad second atomic coordination in nano-hat. The other clusters exhibits second co-ordination widths in agreement with the experimental ones.

The calculation of the free energy of the relaxed molecular clusters gives interesting results.

The lowest free energy cluster is the nano-pie cluster. Thus, the nano-pie seems to be the most stable cluster of the group, and therefore, the most probable to be formed in As_2S_3 glass.

According to Elliott [30] photo-darkening results from photo-induced intra-molecular and/or inter-molecular bond scission. For advanced molecular character of a glass the probability of photo-induced changes by intermolecular and intra-molecular interactions, and thus the photo-sensitivity will increase, too.

Table 1. The free energy of molecular As-S clusters, after energy relaxation.

No.	Molecular cluster	No. of atoms	Distortion energy per atom (10^{-11} J)		
			Bond stretching	Bond bending	Total
1	nano-hat	60	0.55478	9068.5	9069.0
2	nano-pie	180	1.23517	1907.9	1909.2
3	nano-tube	194	157.237	6722.7	6878.9

Preliminary results have shown that packing of several nano-pie clusters, at a Van der Waals distance of 0.385 nm give rise to a diffraction pattern which reproduces fairly well that reported in [29]. The first sharp diffraction peak is very well reproduced. The development of a complex model of As_2S_3 based on packing of various large molecular clusters is in progress.

In conclusion, we have shown, using the modelling procedure at the atomic scale of the stoichiometric arsenic sulphide composition, that large molecular clusters of As_2S_3 are possible without dangling bonds or wrong bonds, being compatible with the requirements of the crystallochemical parameters.

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