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SHORT COMMUNICATION

POSSIBLE NANO-TUBE CONFIGURATIONS IN ARSENIC CHALCOGENIDES

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Modeling of nano-tube clusters based on $As_2S(Se)_3$ has been performed. The structural data were calculated on a single nano-tube model of As_2S_3. For the first time electron microscope images of nanometer size objects in As_2Se_3 and $As_{5.5}Se_{4.5}$ glass have been observed and discussed.

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The structure and properties of the glassy and amorphous chalcogenides are still not completely known [1-6]. In order to have more information on the nanoscale structure of the glass, the X-ray diffraction data must be compared with modeling data, taking into account the possible arrangement of the atoms when appropriate values of the crystallochemical data are taken into account and the corresponding force constants [7] are used in the frame of the valence force field theory [8].

A growing interest was recently paid to fullerene-like objects. The synthesis of fullerene-type and nano-tubes made of inorganic layer materials have been tried. For instance, boron nitride nano-tubes were synthesized [9] and many of the experiments performed on carbon nanotubes were repeated on this system as well [10, 11]. Another class of inorganic nanostructures is represented by the vanadium oxide nano-tubes [12]. Recently, self-assembled single-wall sub nanometer-diameter molybdenum disulphide tubes (n-MoS_2) were prepared and investigated [13, 14].

We have built and energy relaxed a nano-tube configuration of an As_2S_3 cluster in two cases: a nano-tube with open ends (dangling bonds to the ends) and the same nano-tube with closed ends. In the latter case no dangling bonds were permitted in the cluster structure. The coordinates and the table of coordination were carefully recorded and the final energetically relaxed structure was calculated in the frame of a Monte Carlo procedure, using the appropriate force constants known from the literature [7], and the bonding distances and bonding angles from the crystalline counterparts.

Fig. 1 shows the image of a non-relaxed nano-tube of As_2S_3 with open ends, built from plastic units (214 atoms).

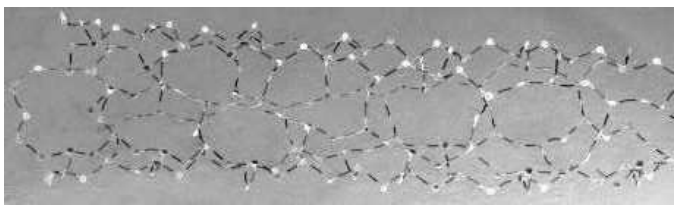

Fig. 1. The picture of the initial (not relaxed) open-end model of a single nano-tube, based on binary As_2S_3 (or As_2Se_3) chalcogenide.

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The model simulates a single nano-tube of As_2S_3 with a diameter of ~1.5 nm, and a length of ~6.2 nm. Fig. 2 shows the bond angle distribution, the bonding distance distribution and the pair distribution function corresponding to the relaxed structure of the nano-tube without and with closed ends.

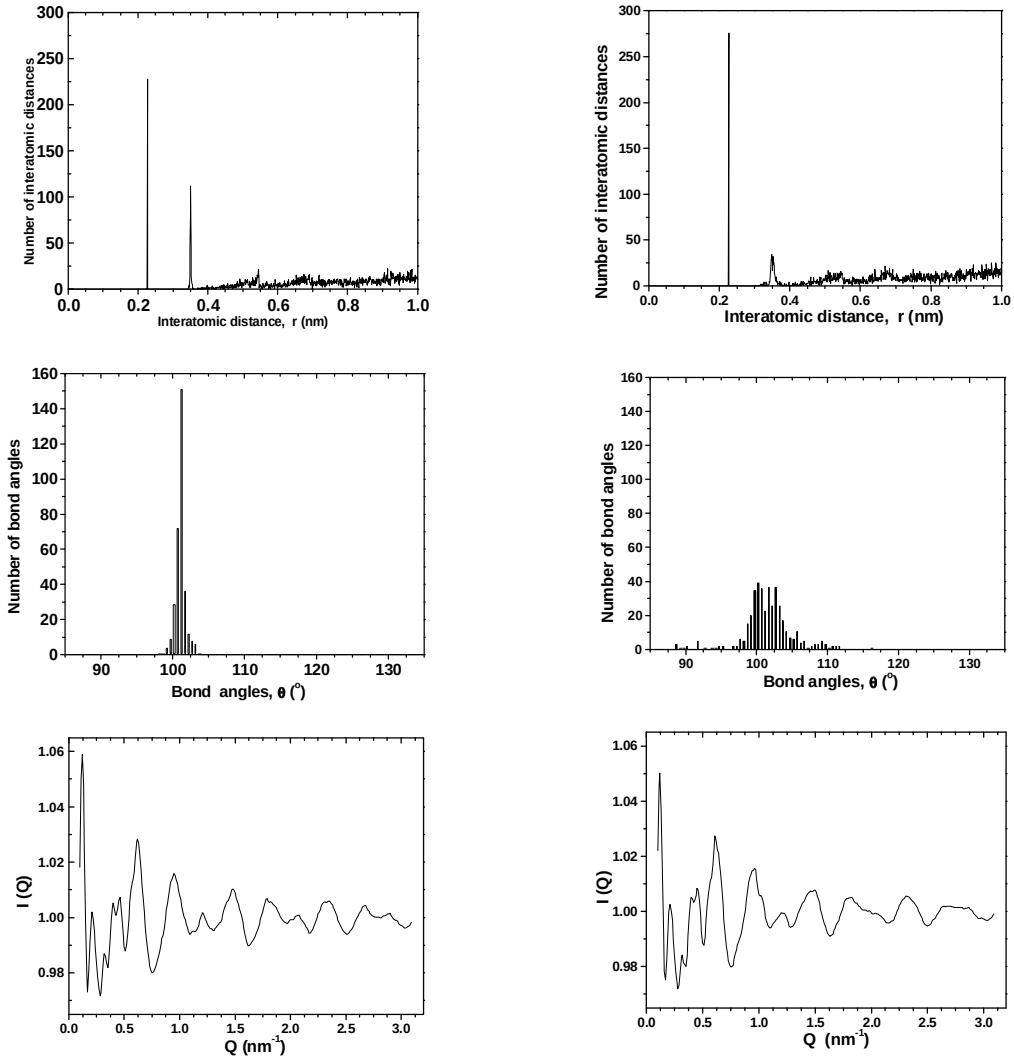

Fig. 2. Pair distribution functions, bonding angle distributions and interference patterns calculated for a single nano-tube with open ends (left side) and with closed ends (right side).

The bond angle distribution is quite narrow in the nano-tube with open ends, but much larger in the nano-tube with closed ends. This means that nano-tubes with open ends are more favourable, because the total free energy is lower in this case. No important differences are observed between the calculated diffraction patterns of the open ends and closed ends nano-tubes.

We have performed, also, an electron microscopy study on As_2Se_3 and $As_{5.5}Se_{4.5}$ glass powders (Fig. 3).

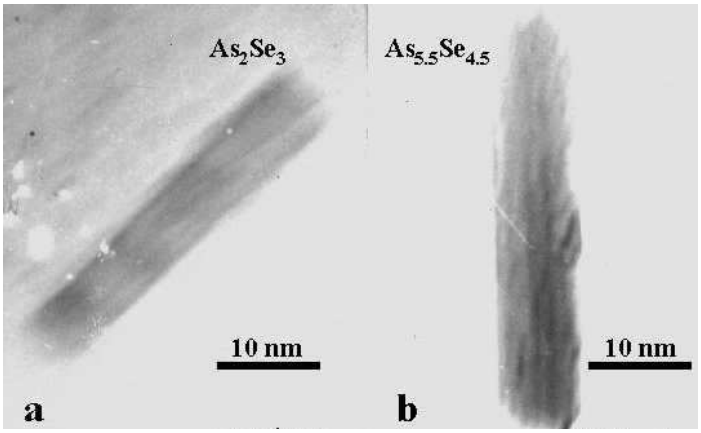

Fig. 3. Electron microscopy images of As_2Se_3 and $As_{5.5}Se_{4.5}$ sticks of nanometer size.

Remarkable whisker-like nano-objects (length: ~ 38-40 nm, diameter: ~ 6-8 nm) could be observed, which might be thought as being built-up of nano-objects like those modeled by us (Fig. 1). There are also extended dark- and light-gray regions of ~ 3 nm size to be observed, alternating along the axis direction of the nano-object (Fig. 3.a). Other details, as e.g. very thin strips of width ~1 nm are seen on the micrographs.

In our opinion, the structure observed in the electron microscope image could be a nano-tube packing of the atoms, eventually with nano-tubes made of two or more rolled-up sheets (onion – like nanotubes).

In conclusion, we have modeled for the first time the structure of a chalcogenide nano-object with the shape of a nano-tube (similar to those found in carbon nano-tube configurations). The arsenic chalcogenide nano-tubes seem to be realistic configurations, because the energetical relaxation in the frame of the valence field theory allows for getting the correct angles, distances and pair distribution functions as known from the crystalline structure of these materials. The results seem to be supported by the electron microscopy images.

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