STRUCTURAL CHARACTERISTICS AND SOME CONCEPTS RELATED TO SWITCHING PROPERTIES IN $As_{0.45}Se_{0.10}Te_{0.45}$ GLASSY ALLOY

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A structural model of the bulk $As_{0.45}Se_{0.10}Te_{0.45}$ amorphous alloy has been built by the random Monte Carlo technique. The model is in good agreement with the atomic radial distribution function obtained by X-ray diffraction. The mean coordination number obtained was 2.3, thus allowing the sample to be characterized as a bistable material.

Chalcogenide glasses are studied mainly because they present a switching phenomenon and a memory effect, and therefore can be used in the making of a great number of electronic devices [1].

The main interest in the analysis of the glass system As–Se–Te [2,3], amongst other reasons, is the dependence of the electrical conductivity on sample composition, as well as presenting memory effect together with the switching process.

For these reasons, a structural analysis as well as an electrical study of the glassy alloy $As_{0.45}Se_{0.10}Te_{0.45}$ has been undertaken, given that the establishment of the structural units, the distribution of chemical bonds between atoms, the radii of the coordination spheres and the mean values of the bonds, besides being of intrinsic interest, allows the process of electrical conductivity to be explained, as it is closely linked to the type and amount of chemical bonds existing in the material.

The $As_{0.45}Se_{0.10}Te_{0.45}$ composition was prepared so that the influence of the amount of Te could be observed, previous studies having been carried out with a smaller atomic fraction of Te [2,3]. Electrical resistance measurements of the composition with a greater amount of Te indicate that it reduces electrical resistance, due to the dislocation of covalent bonds as a result of the metallization of the chemical bond. Analogous behaviour has been reported in the literature [4].

The number of bonds between each of the elements, together with their ionization energies, allows the possibility of forecasting its electrical characteristics in an approximative manner. As electrical resistance is reduced, according to observations drawn from other compositions of this system, it seems likely that the threshold voltage (the minimum voltage needed to produce switching) must also be reduced.

Another characteristic seen in the structural analysis is the degree of stability of the material. The mean coordination number is an indication of the flexibility and elasticity of the composition's structure, closely related to structural changes and therefore to bistable behaviour [1].

The bulk samples of the glassy alloy $As_{0.45}Se_{0.10}Te_{0.45}$ were obtained from the constituting elements, prepared as described in ref. [2].

Fig. 1 is a graphical representation of the radial distribution function of the glassy alloy, obtained from X-ray diffraction data of the compound after having eliminated that part of the radiation not providing structural information. The information set out in table 1 has been obtained from this function.

One of the data shown in table 1 is the area below the first RDF peak, representing the mean number of atoms surrounding an arbitrary reference atom, i.e. the mean coordination number. This datum provides a parameter which allows the estimation of the short-range order in the material.

The area mentioned may be expressed as a function of N coordination, attributed to a specific element in

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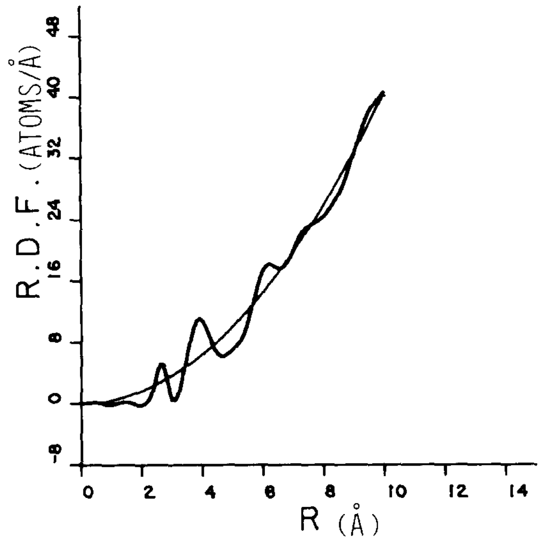

Fig. 1. Radial distribution function.

the alloy and the number of bonds between certain type of pairs, according to the relation deduced by Vázquez et al. [5]:

$$\text{area} = \frac{1}{100(\Sigma_j x_j Z_j)^2}\,[Z_2(\alpha Z_2 + 2\gamma Z_3) + [h + Z_2(\beta Z_2 - 2\delta Z_3)]N + 2(Z_2 - Z_3)^2 a_{33}], \quad (1)$$

where h, α, β, γ and δ are specific characteristics of the compound, as they only depend on the concentration of each element in the compound, on the corresponding atomic number and their coordination.

On the basis of the results from the analysis of the structural models obtained for other compositions of the As–Se–Te system [2,3], structural units have been postulated to generate the theoretical short-range order of the $As_{0.45}Se_{0.10}Te_{0.45}$ alloy, considering that the N coordination of the As in the glassy alloy may be three or four.

Table 1
Peak positions and area under the peaks of the RDF. Errors are estimated

Peak	r (Å)	Area (atoms)	Δ
first	2.65	2.30	0.1
second	3.90	6.94	0.2

The parameters of the compound under study, which are independent of the value postulated for the coordination of one species in the alloy, were:

$h = 48251.25, \quad \alpha = -155.91,$

$\beta = 28.64, \quad \gamma = 200.45, \quad \delta = 36.82.$

From these, by means of expression (1), the area under the first peak in the RDF was determined, which when considered $N = 3$, is:

$\text{area} = 2.2024 + 0.0037\,a_{33}$

and for the hypothesis of tetracoordinated As, $N = 4$, is:

$\text{area} = 1.9208 + 0.0037\,a_{33}.$

As is seen, they are linear functions only dependent on a_{33}, the number of Te–Te bonds in the alloy.

A comparison of these theoretical expressions with the experimental value obtained for the area shows that a short-range model based on tetrahedric As for this alloy cannot be accepted, as a value not included in the estimated error range would be obtained.

Therefore, in this case, a local order model is proposed, based on tricoordinated As atoms, in which As–As bonds are admitted, given the high proportion of this element in the compound.

To establish the theoretical structural model, an initial atomic configuration was generated according to the conclusions drawn from the short-range order analysis of the material, which, as has been described previously, are:

(1) three-fold As coordination;

(2) the possibility of bonding between all the atomic species present in the material.

Bearing in mind that the RDF is a function depending only on the distance, r, to an origin reference atom, the volume limited by a spherical surface with a radius of 10 Å was used, as a geometrical space for generating the positions. This volume had to be large enough to represent the sample appropriately, from a statistical viewpoint, and small enough so that computation time would not be too great.

In agreement with the experimental density of 5.27 g cm^{-3}, with relative error less than 3%, 134 atomic positions were generated by means of an aleatory method, each being admitted if it obeyed the geometrical and coordination conditions, deduced previously from the experimental RDF. In the present case these are:

(i) the distance between first neighbours must be within the interval (2.20–3.05 Å), defined by the first peak of the radial distribution function;

(ii) the bonding angle between an atom and two others in its immediate vicinity may vary between 60 and 180°;

(iii) the maximum number of first neighbours must not be greater than three.

Adjustment of positions was carried out after the initial model was determined, by allowing it to evolve through successive atom movements. Movements which implied the breakage of As atom bonds were not allowed, the object being to maintain the coordination of this element.

When 512 movements had been carried out and the standard deviation between the reduced RDFs of the model and those obtained experimentally was 0.0239,

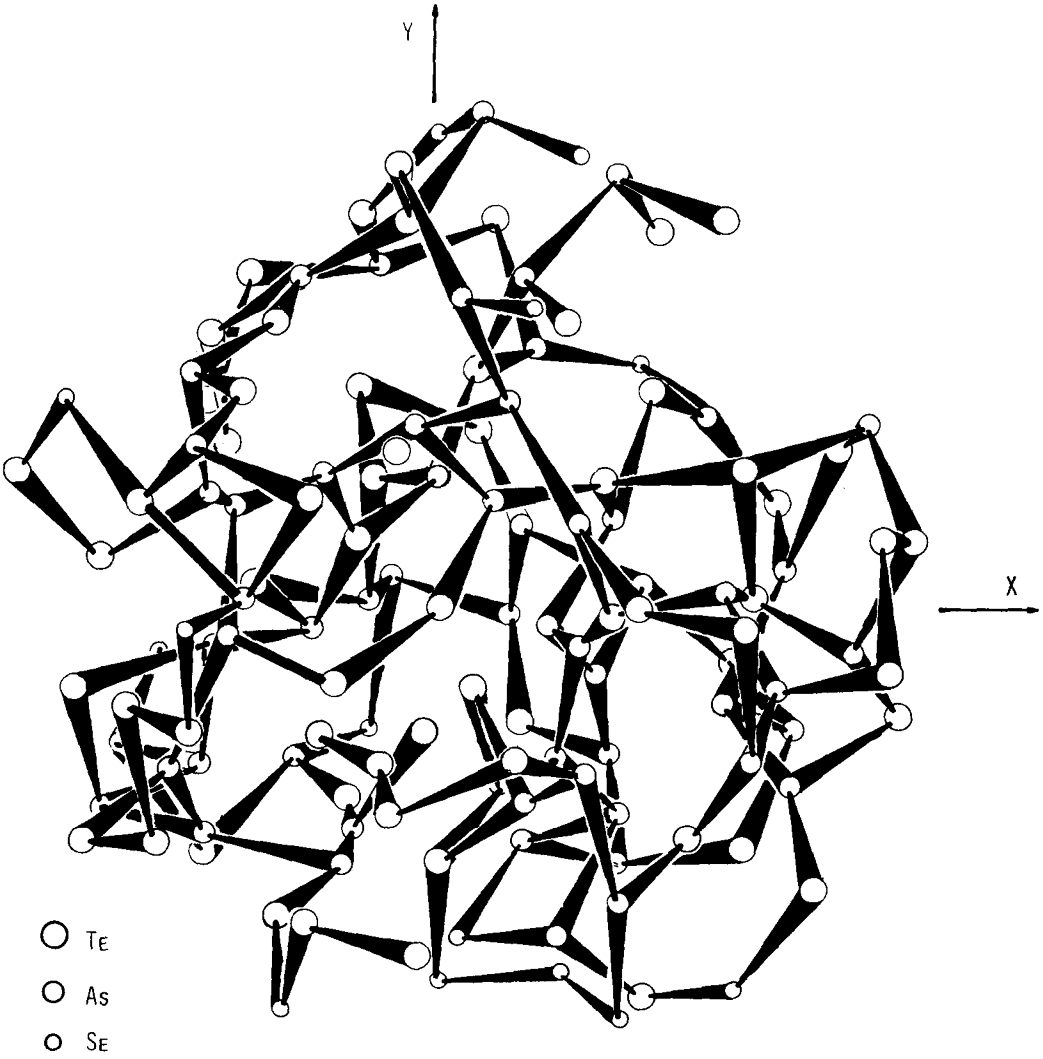

Fig. 2. Spatial representation of the model of $As_{0.45}Se_{0.10}Te_{0.45}$.

Table 2
Model coordinations

Type	Coordination			
	3	2	1	0
As	60(60)	0(0)	0(0)	0(0)
Se	0(0)	11(14)	3(0)	0(0)
Te	9(0)	44(60)	6(0)	1(0)

the adjustment was considered as having been completed, giving the spatial distribution shown in fig. 2.

Table 2 summarizes the coordinations obtained for the different elements in the material, deduced from the generated model. The coordinations corresponding to the postulated model on the basis of the information from the experimental RDF, which has already been indicated, are shown in parentheses.

Table 2 shows coordination defects in the configuration created, which is characteristic of amorphous materials. These defects may be partly justified by the finite size of the model, given that the three Se atoms with coordination one are found less than 2 Å from the surface limiting the model, and of the six Te atoms with coordination one, three are found at less than 1 Å from this surface.

Table 3
Averaged bonding distances (Å)

Bond	Material	$\langle d_{ij} \rangle$	Ref.
As–As	$As_{0.45}Se_{0.10}Te_{0.45}$	2.57	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.59	[3]
	As_4S_4	2.59	[6]
As–Se	$As_{0.45}Se_{0.10}Te_{0.45}$	2.46	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.49	[3]
	As_2Se_3	2.43	[7,8]
As–Te	$As_{0.45}Se_{0.10}Te_{0.45}$	2.58	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.55	[3]
	sum of covalent radii	2.58	[9]
Se–Se	$As_{0.45}Se_{0.10}Te_{0.45}$	2.44	a)
	$As_{0.20}Se_{0.50}Te_{0.30}$	2.45	[3]
	amorphous Se	2.40	[10]
Se–Te	$As_{0.45}Se_{0.10}Te_{0.45}$	2.58	a)
	$As_{0.40}Se_{0.30}Te_{0.30}$	2.55	[2]
Te–Te	$As_{0.45}Se_{0.10}Te_{0.45}$	2.67	a)
	$As_{0.40}Se_{0.30}Te_{0.30}$	2.60	[2]
	$Al_{0.23}Se_{0.77}$	2.71	[11]

a) This paper.

One way of estimating the agreement between the generated model and the real structure of the alloy under study, is by analyzing the structural parameters, bonding distances and bonding angles, obtained from the model, relating their values with those given in the literature for similar compounds.

Table 3 shows the mean bonding distance between the different pairs of elements. It is seen that the values calculated for the bonding distances show good agreement with data from the literature. Table 4 shows the mean bonding angles obtained from the model generated at random representing the $As_{0.45}Se_{0.10}Te_{0.45}$ alloy.

From the reports by S.R. Ovshinsky [1] on the mean coordination numbers of two types of materials destined for the making of electronic devices, i.e. threshold or unistable, and memory or bistable, it is deduced that the glassy composition $As_{0.45}Se_{0.10}Te_{0.45}$ presents the typical characteristics of memory materials [14]. The criterion used establishes that unistable materials have a mean coordination number of approximately 2.9, while in bistable materials it is very close to 2.3. These values are remarkably different, which explains the different physical characteristics of each one. The parameter indicating the num-

Table 4
Averaged bonding angles (deg)

Type	$\langle \alpha \rangle$	Material	Ref.
As	108.2	$As_{0.45}Se_{0.10}Te_{0.45}$	a)
	109.5	$As_{0.20}Se_{0.50}Te_{0.30}$	[3]
	109.9	$As_{0.40}Se_{0.30}Te_{0.30}$	[2]
	107.1	AsSe glass	[12]
Se	107.7	$As_{0.45}Se_{0.10}Te_{0.45}$	a)
	105.5	$As_{0.20}Se_{0.50}Te_{0.30}$	[3]
	106.7	$As_{0.40}Se_{0.30}Te_{0.30}$	[2]
	107.5	Se glass	[12]
Te	107.0	$As_{0.45}Se_{0.10}Te_{0.45}$	a)
	104.6	$As_{0.20}Se_{0.50}Te_{0.30}$	[3]
	104.7	$As_{0.40}Se_{0.30}Te_{0.30}$	[2]
	102.0–109.5	TeGe glass	[13]

a) This paper.

ber of atoms within the first coordination sphere is the area under the first peak of the RDF. In this case, the value is 2.30 atoms, which justifies the electrical characterization carried out previously, that is to say, the structure type of this material allows easy crystallization.

Thus, the RDF obtained from X-ray diffraction studies throws light on the possibilities of a specific material destined for the manufacture of electronic devices.

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