Ge–As–Te GLASSY SYSTEM. ATOMIC DISTRIBUTION MODELS

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Received 21 April 1987

Atomic structure models were generated for the semiconducting glassy alloys $Ge_xAs_{0.20}Te_{0.80-x}$ ($x=0.05$, 0.10), from short-range order information given by the corresponding radial distribution functions, obtained from X-ray diffraction intensities. The Metropolis Monte Carlo random method was used in the building of the models, and the fact that Ge atoms can be four- and three-coordinated has been taken into account. The structural parameters obtained from the models agree with those given in the literature for similar alloys.

Understanding of the atomic peaking of solids in general, and amorphous materials in particular, allows one to correlate their physical properties to their atomic structure.

The Ge–As–Te glassy system exhibits electrical properties such as the switching phenomenon and the memory effect [1–4]. These materials are useful for making electronic devices due to properties such as these [5]. In this work, atomic structure models of the alloys $Ge_{0.05}As_{0.20}Te_{0.75}$ (MI) and $Ge_{0.10}As_{0.20}Te_{0.70}$ (MII), belonging to the above-mentioned system, have been built, using the Metropolis Monte Carlo random method, suitably modified [6,7].

The bulk samples were obtained by the melt–quench method. Suitable amounts of the elements Ge, As and Te, of a nominal purity of 5N, were weighed, sifted, mixed and introduced into vacuum-sealed quartz ampoules. The sealed ampoules were put into a rotary furnace at a temperature of 1000°C for one day, and finally quenched in an ice–water bath. The glassy nature of these materials was confirmed by X-ray diffraction. The resulting X-ray diffraction patterns did not present the peaks characteristic of crystalline materials.

The X-ray diffraction intensities were measured by an automatic Siemens D500 diffractometer with Bragg–Brentano geometry, by reflexion, equipped with a bent graphite monochromator and a scintillation counter. The radiation used was Mo Kα ($\lambda=0.71069$ Å). The radial distribution function (RDF) was determined for each of the alloys using the obtained intensities, suitably corrected [8].

The analysis of these functions has allowed us to know the short-range order of these materials, which has given us a starting point for building structural models of both alloys, using the Metropolis Monte Carlo random method with the appropriate restrictions. These restrictive conditions refer to geometry and coordination.

The two geometric restrictions taken into account in the making of each model were deduced from the RDFs of the alloys. The first one refers to the distance between first neighbours, and is determined by the definition limits of the first RDF peak. This interval is (2.35 Å, 3.05 Å) for alloy MI, and (2.40 Å, 3.10 Å) for alloy MII. The second one refers to the bond angle variation intervals, also determined from the experimental RDFs, and which are (70°, 180°) for sample MI and (68°, 136°) for sample MII.

As to the coordination restriction, the criteria established for amorphous alloys containing Ge, in which values of 3 and 4 are considered as possible coordination for this kind of atom [8,9], have been followed. In our previous study [10], it has been proven that the atomic structure model of the amorphous alloy $Ge_{0.14}As_{0.43}Te_{0.43}$, belonging to this sys-

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Table 1
Atomic distribution in the generated models

Alloy	Experimental density (g/cm^3)	N	Number of atoms		
			Ge	As	Te
MI	5.72	126	6	25	95
MII	5.66	127	12	25	90

tem, in which four- and three-coordinated Ge atoms coexisted, was the one that best fits the RDF obtained experimentally by X-ray diffraction. In the present paper, we have taken this hypothesis as a basis for building the atomic models of the alloys studied.

In order to make these models it is necessary to choose the shape and dimensions of the volume in which they are going to be located. Bearing in mind that the radial distribution function only depends on r, the distance from an atom taken as a reference point, the models have been generated inside spheres with a radius of 10 Å [11].

Due to the low coordination presented by the models generated from a number of positions equal to the number of atoms predicted from the experimental density of the materials, 200 positions were created initially, a value higher than the number of atoms, N, obtained for each alloy from their respective experimental densities, ρ_0. Table 1 shows the values of these parameters for each of the alloys, together with the number of each kind of atom that comprises the model according to the atomic composition of each sample.

The 200 positions generated were reduced to N by eliminating those which exhibit the lowest coordination, and atoms were then assigned to them in a semi-random way, with the Ge atoms taking 4- or 3-coordination positions, so that the previously established hypotheses would be complied with [8–10].

The reduced radial distribution functions, $rG_{\mathrm{mod}}(r)$, were obtained for each of the initial configurations and compared to the experimental ones, $rG_{\mathrm{exp}}(r)$, for each of the alloys, suitably modified by the finite size simulation function [12]. Mean-square deviation, ϵ^2, between the $rG_{\mathrm{mod}}(r)$ and the $rG_{\mathrm{exp}}(r)$ was 2.0941 Å and 1.8914 Å for samples MI and MII, respectively. These values were considered adequate in order to take the initial configurations as valid, to proceed to refining them and obtain representative models of the atomic structures of these alloys.

Table 2
Position refining process for both models

Alloy	P (Å)	Movement intervals	Squared deviation (Å)
MI	0.5	1–359	0.0672
	0.3	360–435	0.0386
	0.1	436–546	0.0256
MII	0.5	1–359	0.0668
	0.3	360–435	0.0379
	0.1	436–533	0.0229

The atomic position refining process was carried out using the Metropolis Monte Carlo technique [6], which consists basically of randomly modifying the initial position of a random atom. The new position is accepted if the restrictions imposed by the experimental RDF (definition interval of the first peak, and bond angle variation interval) are met, and at the same time the mean-square deviation between functions $rG_{\mathrm{mod}}(r)$ and $rG_{\mathrm{exp}}(r)$ decreases.

When this technique is used, the amplitude, P, of the atomic movements is arbitrarily fixed and may be modified throughout the refining process, in order

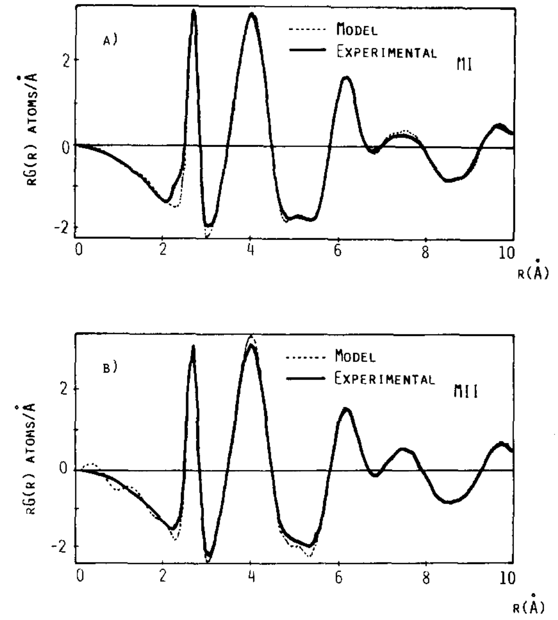

Fig. 1. Representation of calculated and experimental RDFs for both alloys.

to achieve quicker convergence. Following ref. [13], the values taken for P varied between 0.5 Å, at the beginning of the refining process, and 0.1 Å at the end. During the refining process, the two models evolved as shown in table 2, in which the mean-square deviation refers to the last movement in each interval. The position refining process was considered finished when the number of rejected movements was too high, and the mean-square deviation did not sensibly improve.

Once the position refining process was finished, the thermal factor refining process began, the corresponding coordination spheres being defined from the experimental RDFs, and $\sigma_0 = 0.1$ Å being taken as the initial value of the isotropic factor. The series of values of σ_i which best adjust the reduced RDF of each model to the experimental RDF were calculated by an iterative least-squares method. Once the process was finished, the values of the mean-square deviations were 0.0247 Å for alloy MI and 0.0217 Å for alloy MII, and fig. 1 shows the reduced RDFs for each of the compounds studied.

The theoretical models built by random techniques, and bearing in mind the structural information obtained from the radial distribution functions of the samples, must be as representative

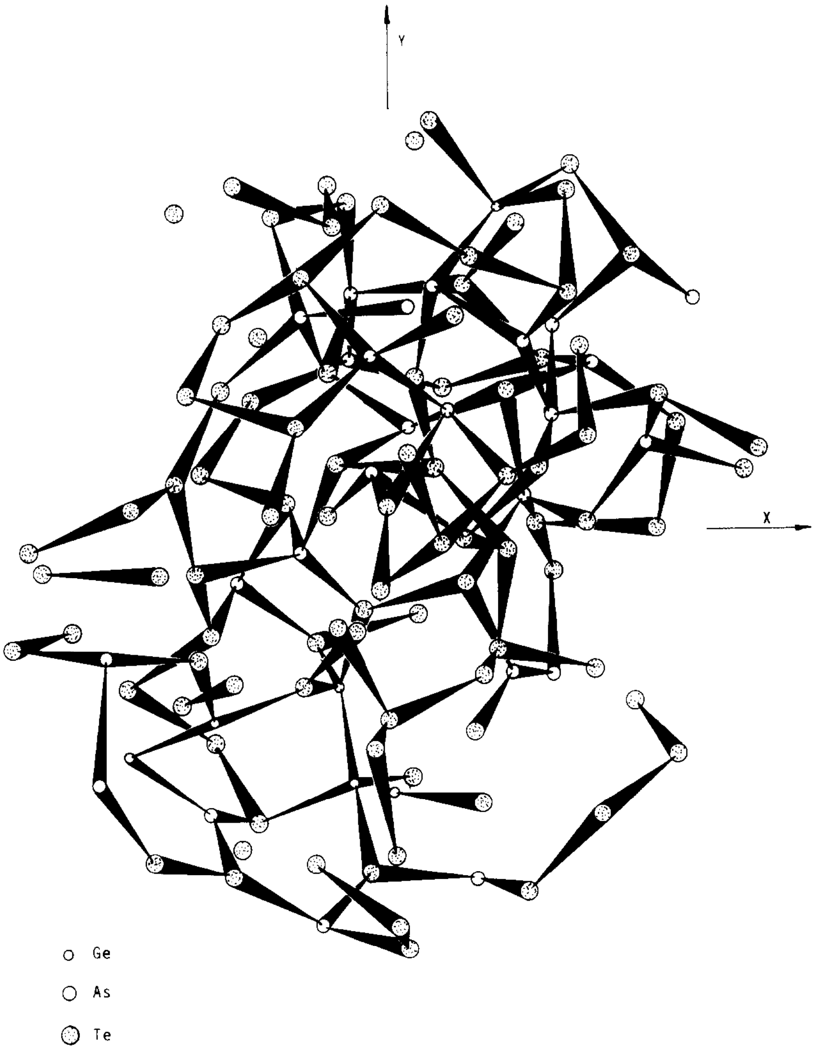

Fig. 2. Spatial representation of the model of $Ge_{0.05}As_{0.20}Te_{0.75}$ alloy.

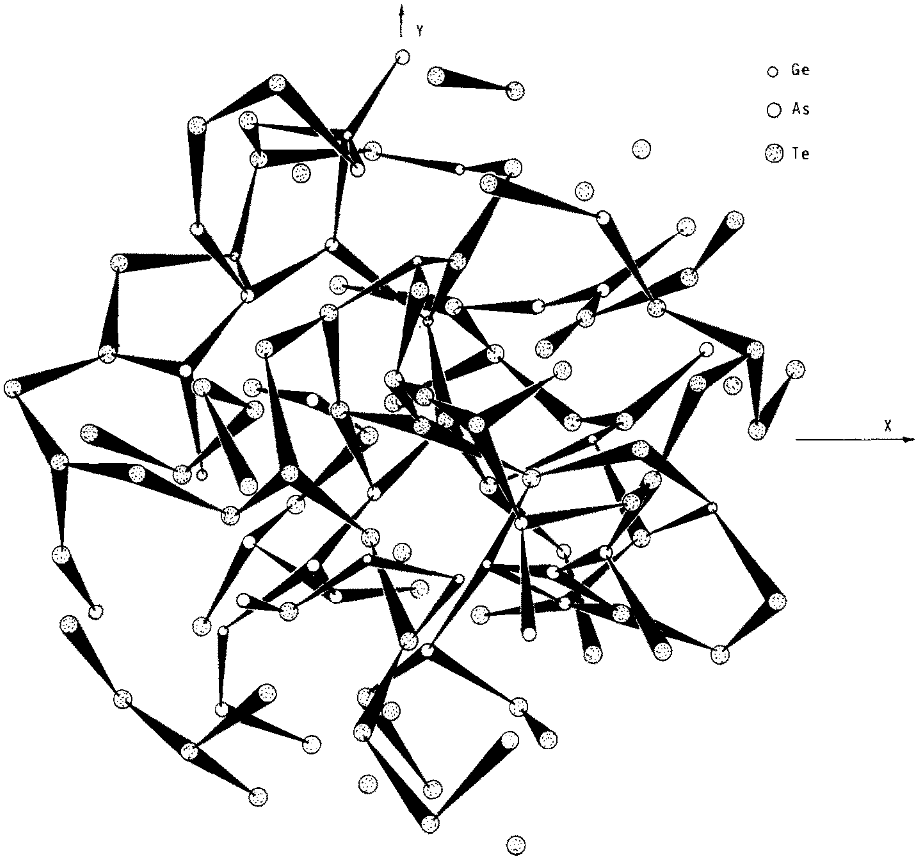

Fig. 3. Spatial representation of the model of $Ge_{0.10}As_{0.20}Te_{0.70}$ alloy.

as possible of the actual structure of the compounds studied. One way to estimate the degree of agreement between the abovementioned models and the true structure of the alloys consists of analyzing the main structural parameters (coordinations; bond lengths and angles) which may be inferred from them, and relating their values to those cited in the literature for other compounds similar to those being studied.

Figs. 2 and 3 show the spatial representations of the atomic models built, and table 3 shows the coordinations found in these models, for each of the elements in the alloys. Dangling bonds are observed in both models, most of which could be explained by the finite size of the models.

The following criterion has been established: Atoms which are less than a first-neighbour distance away from the spheric surface that encloses the model do not present bond defects, as they could saturate their bonds with hypothetical atoms located outside the surface. 11% of the bond defects exhibited by alloy MI, and 19% of those exhibited by alloy MII,

Table 3
Number of atoms with their coordination in each model

Alloy	Atom	Coordination				
		4	3	2	1	0
MI	Ge	3	1	1	1	0
	As	6	13	4	2	0
	Te	0	30	35	26	4
MII	Ge	2	5	4	1	0
	As	2	11	7	5	0
	Te	0	23	34	25	8

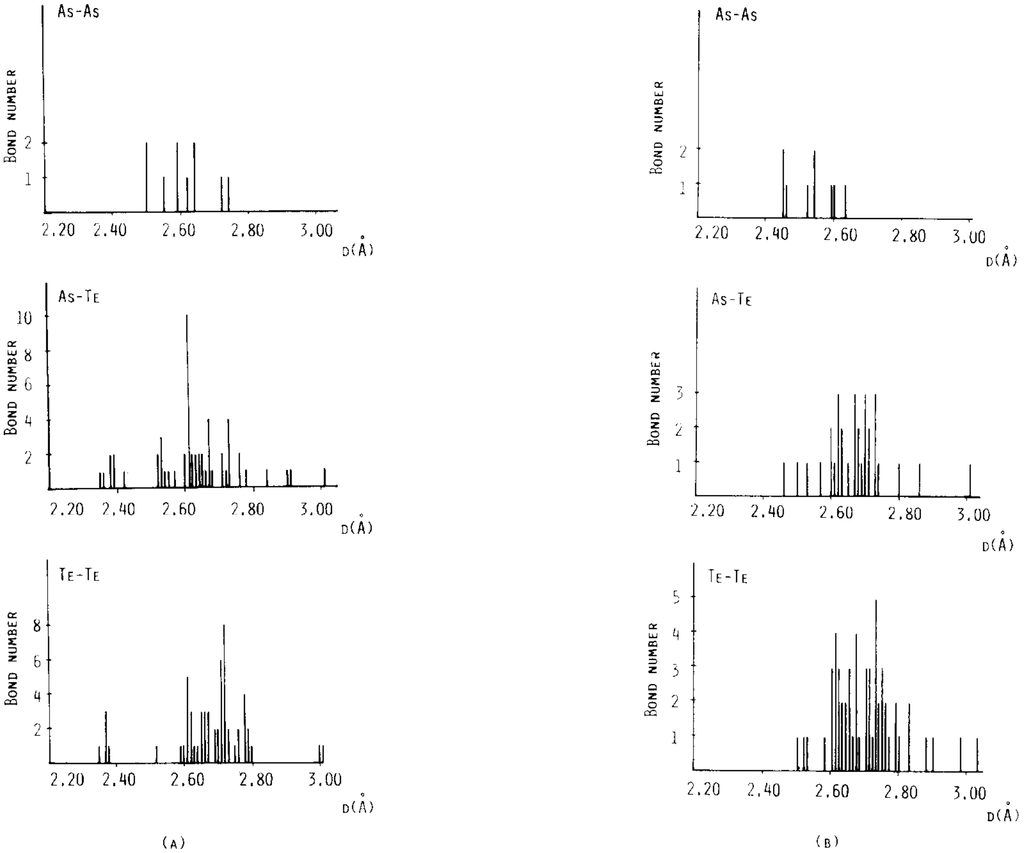

Fig. 4. Histograms of the distances in the pairs of elements As–As, As–Te and Te–Te. (a) Model of alloy MI, (b) model of alloy MII.

cannot be explained by the finite size of the models. In any case, coordination defects are inherent to this type of alloy, due to the sample preparation method.

Another important parameter for the evaluation of the degree of validity of the models is the bond length for each pair of elements which constitute the materials, because it shows the agreement between the theoretically calculated lengths in the structures sought and the ones already known for other similar compounds.

Fig. 4 shows the bond length histograms of the pairs of elements As–As, As–Te and Te–Te for each of the generated models. The histograms of the other pairs of elements have not been done, due to the small amount of Ge in the studied compounds and its low representativity from a statistical point of view.

Table 4 shows the mean bond lengths between the different pairs of elements, for each of the models of alloys MI and MII, together with the corresponding lengths quoted in the literature. It may be observed in table 4 that the Ge–As bond lengths, for both alloys, differ remarkably from those found in the literature, although these differences should not be taken into consideration because of the small number of these bonds present in the models. The rest of the theoretically calculated bond lengths are in good agreement with the bibliographical data, as they do not differ in more than 1%.

Table 5 shows the mean bond angles obtained from the generated models of each alloy, together with those quoted in the literature. There is good agreement in the data found, although one must bear in mind that bond angle deformation is a characteristic of glassy materials, due to the tensions created in the material as a consequence of its metastable energetic state.

Table 4
Average bonding distances (Å)

Bond	$\langle d \rangle$	Ref.
Ge–Ge	2.46	MI
	2.53	MII
	2.46	[14]
	2.53	[10]
Ge–As	2.69	MI
	2.66	MII
	2.47	[10]
	2.45	[15]
Ge–Te	2.65	MI
	2.63	MII
	2.59	[10]
	2.60	[16]
	2.67	[17]
As–As	2.61	MI
	2.55	MII
	2.59	[13]
	2.57	[11]
	2.56	[10]
As–Te	2.63	MI
	2.67	MII
	2.66	[17]
	2.65	[18]
	2.61	[10]
Te–Te	2.67	MI
	2.70	MII
	2.67	[11]
	2.71	[19]

Table 5
Average bonding angles (deg)

Type	$\langle \alpha \rangle$	Ref.
Ge	107.5	MI
	110.2	MII
	111.9	[10]
	108.2	[20]
As	107.3	MI
	113.3	MII
	107.1	[21]
	109.2	[22]
Te	108.2	MI
	109.9	MII
	108.4	[13]
	110.9	[22]

As a result of the study carried out, we may conclude that the atomic structure of these alloys can be described as a three-dimensional network formed by tetrahedric and pyramidal structural units, where the Ge atoms occupy the centres of the tetrahedra, in the former case, and one of the vertexes of the triangular pyramids, in the latter. These structural units are joined together either by As and Te atoms or by chains of these atoms, forming a compact network.

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