



## On the structure of Ge–As–Te–Cu glasses



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### ABSTRACT

Short range order in glassy  $0.9(\text{Ge}_{0.1}\text{As}_{0.15}\text{Te}_{0.75})-0.1\text{Cu}$  (GATC1) and  $0.9(\text{Ge}_{0.05}\text{As}_{0.55}\text{Te}_{0.4})-0.1\text{Cu}$  (GATC2) was studied by neutron- and X-ray diffraction as well as EXAFS (extended X-ray absorption fine structure) measurements at the K-edges of all components. The reverse Monte Carlo simulation technique was used to create models consistent with all experimental datasets. It was found that Cu binds predominantly to Te in GATC1 while Cu–As and Cu–Cu bonding is also significant in GATC2. Ge and As atoms have 4 and 3 Ge/As/Te neighbors in both compositions. In GATC1 the formation of ‘extra’ Te–Te bonds can be observed, similarly to  $\text{GeTe}_4\text{–AgI}$  glasses.

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### 1. Introduction

As–Te alloys can be vitrified over a broad composition range (~20–60 at.% As). A detailed study of As–Te glasses by diffraction techniques and EXAFS revealed that they could be considered as random covalent networks, without any type of preferred bonding [1–3]. The Ge–Te system behaves in a completely different way: liquid Ge–Te alloys can be vitrified only in the vicinity of the eutectic composition (15–20 at.% Ge). A reverse Monte Carlo simulation study using EXAFS and diffraction datasets showed that Ge–Ge bonding is not significant in these glasses [4]. Later this finding was confirmed by EXAFS and X-ray photoelectron spectroscopy [5]. Given the sensitivity of the experimental techniques applied it means that the Ge–Ge coordination number is not higher than ~0.3, thus amorphous Ge–Te alloys around the eutectic composition should be regarded as chemically ordered.

Ge–As–Te (GAT) alloys can be vitrified between ~80% and ~35% Te content. The different behaviors of As and Ge in binary tellurides are also inherited by the ternary glasses. There is a pronounced ordering around Ge atoms, which prefer Te to As and Ge while As–As bonding is significant even in Te-rich compositions (e.g.  $\text{Ge}_{10}\text{As}_{15}\text{Te}_{75}$ ) [6].

Glass formation in the Ge–As–Te–Cu (GATC) system has been reported recently [7]. GATC glasses have excellent transmission in the IR range and possess high conductivity. This favorable combination of properties makes them suitable for detecting charged biomolecules by electrodepositing them and measuring their IR spectra.

The aim of the present study is the determination of the short range order in GATC. Comparison of the structure of GAT and GATC glasses reveals how Cu atoms modify the Ge–As–Te covalent network. This question is especially interesting because glassy tellurides can host modifiers by entirely different mechanisms. For example, in  $0.75\text{GeTe}_4-0.25\text{AgI}$  the total coordination number of Te is close to 3 and the sum of Te–Ge and Te–Te coordination numbers is 2.76 [8]. Therefore, in this case Ag and I induce a strong rearrangement of the Ge–Te covalent network. On the other hand, in Ge–Ga–Te [4] and Te-rich Ge–Cu–Te [9] glasses the sum of Te–Te and Te–Ge coordination numbers remains close to 2 but the total coordination number of Te is significantly higher than 2, showing that modifying atoms form additional bonds with Te but do not rearrange the host network.

Chemical short range order in an alloy can be characterized by the partial pair correlation functions. The number of these functions in case of an  $n$ -component system is  $n(n+1)/2$ . As four-component glasses have ten partial pair correlation functions the detailed description of the short range order of Ge–As–Te–Cu glasses is a rather challenging goal. Close distances (e.g. Ge–Te, As–Te, Cu–Te) can be

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separated reliably only by combining various experimental techniques. For this reason we have carried out neutron and X-ray diffraction experiments as well as EXAFS measurements at the K absorption edges of all components. Large scale structural models have been created by fitting simultaneously the 6 experimental datasets in the framework of the reverse Monte Carlo simulation technique [10,11]. Besides fitting experimental data, this method is also capable of incorporating existing physical and chemical information (e.g. density, preferred coordination numbers, chemical ordering) in the models created. The use of various constraints also gives the possibility of estimating the uncertainty of coordination numbers or assessing the validity of various structural models, in general.

## 2. Sample preparation

Both glass samples were prepared using high purity elements (99.999% Ge and Cu, 99.9999% As, and 99.9999% Te) introduced in a silica ampoule which was flame sealed under high vacuum. The melt was homogenized for 8 h in a rocking furnace at 850 °C. After homogenization, the temperature of the furnace was lowered to 600 °C to reduce the vapour pressure and after an isothermal heating for 1 h the ampoule was quenched in water. The ampoule containing the glass was then immediately annealed at 20 °C below the glass transition temperature  $T_g$  for 3 h. The resulting glass rod was recovered by breaking the silica ampoule.

## 3. Experimental

The neutron diffraction experiment was carried out at the 7C2 liquid and amorphous diffractometer of the Laboratoire Léon Brillouin (Saclay, France). Powdered samples were filled into thin walled vanadium sample holders (diameter: 6 mm, wall thickness: 0.1 mm).  $0.9(\text{Ge}_{0.1}\text{As}_{0.15}\text{Te}_{0.75})-0.1\text{Cu}$  was measured with the old 'banana' detector filled with  $\text{BF}_3$ . The new  $^3\text{He}$ -filled detector system was used to measure  $0.9(\text{Ge}_{0.05}\text{As}_{0.55}\text{Te}_{0.4})-0.1\text{Cu}$ . Raw data were corrected for background scattering and detector efficiency. The offset of the detector position and the wavelength of the incident neutron beam (0.72 Å) were determined by measuring a Ni standard.

The X-ray diffraction and EXAFS experiments are described in ref. [6].

## 4. Reverse Monte Carlo simulation

The reverse Monte Carlo simulation technique was used to generate particle configurations fitting all experimental datasets and using available physical information. Simulation boxes contained 20,000 atoms.

Density measurements of  $\text{Ge}_{15}\text{Te}_{85}$ -Cu glasses [12] revealed that the partial molar volume of the  $\text{Ge}_{15}\text{Te}_{85}$  host matrix (i.e. the volume in which 0.15 mol Ge and 0.85 mol Te can be found) does not depend significantly on the Cu content (up to 10 at.%). Molar volume of GATC1 was therefore estimated by multiplying the molar volume of  $\text{Ge}_{10}\text{As}_{15}\text{Te}_{75}$  [6] by 0.9. Similar measurements showed that the partial molar volume of  $\text{As}_{50}\text{Te}_{50}$  is ~1.8% greater in  $\text{As}_{50}\text{Te}_{50}$ -10%Cu than in the undoped binary glass [12]. It is reasonable to assume that the 'breathing' of the host matrix increases with decreasing Te content due to the decreasing average distance of the atoms. Thus the molar volume of GATC2 was taken to

**Table 1**

Estimated molar volumes (in  $\text{cm}^3$ ) of GATC1 and GATC2 used in the reverse Monte Carlo simulation. The values of the corresponding undoped glasses [6] are also given for comparison.

GATC1	18.32
$\text{Ge}_{10}\text{As}_{15}\text{Te}_{75}$	20.35
GATC2	16.88
$\text{Ge}_5\text{As}_{55}\text{Te}_{40}$	17.96

**Table 2**

Minimum interatomic distances (in Å) used in the reverse Monte Carlo modelling of  $0.9(\text{Ge}_{0.10}\text{As}_{0.15}\text{Te}_{0.75})-0.1\text{Cu}$  and  $0.9(\text{Ge}_{0.05}\text{As}_{0.55}\text{Te}_{0.4})-0.1\text{Cu}$  (values in parentheses).

Ge-Ge	Ge-As	Ge-Cu	Ge-Te	As-As	As-Cu	As-Te	Cu-Cu	Cu-Te	Te-Te
3.6	3.6 (2.35)	3.1	2.35	2.35	3.1 (2.65)	2.35	3.1 (2.45)	2.35	2.5

be only 6% smaller than that of  $\text{Ge}_5\text{As}_{55}\text{Te}_{40}$  (see Table 1). Test runs revealed that small ( $\pm 3\%$ ) changes of the density have no significant effect on short range order parameters.

Minimum interatomic distances are listed in Table 2. Backscattering factors needed to calculate the model EXAFS curves from partial pair correlation functions [13] were obtained by the feff8.4 program [14]. Raw  $\chi(k)$  data were filtered in two steps: first  $k^3\chi(k)$  was forward Fourier-transformed into r-space using a Kaiser-Bessel window ( $\alpha = 1.5$ ). The k-range of transformation was around  $1.8 \text{ \AA}^{-1}$ – $14 \text{ \AA}^{-1}$  for the As and Te K edges and around  $1.8 \text{ \AA}^{-1}$ – $12.5 \text{ \AA}^{-1}$  for the Ge and Cu edges. The resulting r-space data were backtransformed using a rectangular window (usually over the r-space range of  $1.2 \text{ \AA}$ – $3.2 \text{ \AA}$ ). Coordination numbers and nearest neighbor distances are given in Tables 3 and 4 while fits and some partial pair correlation functions are shown in Figs. 1 and 2.

## 5. Results and discussion

### 5.1. $0.9(\text{Ge}_{0.1}\text{As}_{0.15}\text{Te}_{0.75})-0.1\text{Cu}$

First the environment of Ge atoms was investigated. It was found that the elimination of Ge-Ge, Ge-As and Ge-Cu bonds does not influence the quality of fits. Therefore Ge atoms were allowed to have only Te neighbors and the Ge-Te coordination number was constrained to be 4. The Ge-Te bond length ( $2.60 \pm 0.02 \text{ \AA}$ ) is in a good agreement with literature values [4,6,15,16].

Arsenic binds mostly to Te but As-As bonding also improved fit qualities. The total coordination number of As was constrained to be 3.  $N_{\text{AsAs}}$ , the As-As coordination number is  $0.33 \pm 0.2$  which is very close to the corresponding value (0.39) of  $\text{Ge}_{10}\text{As}_{15}\text{Te}_{75}$  glass [6].

Cu has on the average  $3.37 \pm 0.3$  Te neighbors. The mean Cu-Te distance is  $2.56 \pm 0.02 \text{ \AA}$ , which agrees with the value found in amorphous  $\text{GeCu}_2\text{Te}_3$  [17]. It was established that the fit of the Cu K-edge EXAFS data was improved upon allowing Cu-Cu bonding. However, the position of the first peak of  $g_{\text{CuCu}}(r)$ , the Cu-Cu partial pair correlation function, was strongly sensitive to the parameters of the fit (e.g. fitting range, weight of the Cu EXAFS dataset). Therefore it has been concluded

**Table 3**

Coordination numbers of  $0.9(\text{Ge}_{0.10}\text{As}_{0.15}\text{Te}_{0.75})-0.1\text{Cu}$  and  $0.9(\text{Ge}_{0.05}\text{As}_{0.55}\text{Te}_{0.4})-0.1\text{Cu}$  obtained by simultaneous fitting of diffraction and EXAFS datasets. Values in bold were obtained by coordination number constraints, therefore no uncertainty is given.

	GATC1	GATC2
$N_{\text{GeAs}}$	–	$1.80 \pm 0.6$
$N_{\text{GeTe}}$	<b>4.00</b>	$2.20 \pm 0.6$
$N_{\text{AsGe}}$	–	$0.16 \pm 0.05$
$N_{\text{AsAs}}$	$0.37 \pm 0.2$	$1.48 \pm 0.3$
$N_{\text{AsCu}}$	–	$0.28 \pm 0.1$
$N_{\text{AsTe}}$	$2.62 \pm 0.2$	$1.36 \pm 0.3$
$N_{\text{CuAs}}$	–	$1.40 \pm 0.4$
$N_{\text{CuCu}}$	–	$1.91 \pm 0.4$
$N_{\text{CuTe}}$	$3.37 \pm 0.3$	$1.23 \pm 0.4$
$N_{\text{TeGe}}$	<b>0.53</b>	$0.28 \pm 0.08$
$N_{\text{TeAs}}$	$0.52 \pm 0.04$	$1.87 \pm 0.4$
$N_{\text{TeCu}}$	$0.50 \pm 0.1$	$0.35 \pm 0.1$
$N_{\text{TeTe}}$	$1.19 \pm 0.2$	0.03
$N_{\text{Ge}}$	<b>4.00</b>	<b>4.00</b>
$N_{\text{As}}$	<b>2.99</b>	$3.28 \pm 0.1$
$N_{\text{Cu}}$	$3.37 \pm 0.3$	$4.54 \pm 0.3$
$N_{\text{Te}}$	$2.74 \pm 0.2$	$2.53 \pm 0.2$

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