The Cu and Te coordination environments in Cu-doped Ge–Te glasses

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ABSTRACT

The structure of $Ge_{20}Te_{80}$, $Ge_{15}Cu_8Te_{77}$ and $Ge_{15}Cu_5Te_{80}$ glasses was investigated by diffraction techniques and extended X-ray absorption fine structure measurements. Large structural models were generated by fitting experimental data by the reverse Monte Carlo simulation technique. In $Ge_{20}Te_{80}$ glass, both Ge and Te obey the $8 - N$ rule, and the structure is built up of $GeTe_4$ tetrahedra connected via Te–Te bonding or shared Te atoms connected to two Ge atoms. The coordination number of Te is significantly higher than 2 in $Ge_{15}Cu_8Te_{77}$. The average coordination number of Cu is 3.41 ± 1 in this alloy. In $Ge_{15}Cu_5Te_{80}$ glass, Cu binds mostly to Te, while Cu–Cu bonding is significant in $Ge_{15}Cu_8Te_{77}$.

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1. Introduction

Amorphous tellurides are applied in various fields of optics and electronics. Te–Ge–Se and Te–Ge–Ga glasses are used as optical elements of far-IR space telescopes [1,2]. As–Se–Te glasses have found application in waste water technology [3], while high-conductivity Cu-doped Ge–As–Te glasses are suitable for the detection of charged biomolecules [4]. All these materials are characterized by excellent glass-forming ability, which permits the shaping of bulk pieces (lenses, fibers) from the ingots. In contrast with the above applications, DVD and PC RAM technologies are based on the fast and reversible phase change (crystallization/revitrification) of Ge–Sb–Te glasses [5].

Due to their technological importance, and also to the basic scientific interest stimulated by large variations in glass-forming ability, the structure of telluride glasses has been investigated intensely investigated in recent years. Amorphous As–Te [6], Ge–Sb–Te [7,8], Ge–Se–Te, Ge–I–Te, and Ge–Ga–Te [9] materials have been studied by an experiment-based approach, simultaneously fitting diffraction and X-ray absorption fine structure EXAFS measurement datasets by the reverse Monte Carlo simulation technique [10]. It has been found that the $8-N$ rule [11] is always satisfied by germanium, while the coordination number of Te is significantly higher than 2 in some glasses. For example, in

$GeGaTe_7$, the coordination number of Te is 2.36 ± 0.15. It was also observed that the number of Ge and Te atoms around Te is close to 2, which suggests that Ga does not break the bonds of the Ge–Te host matrix but forms extra bonds with Te.

A similar increase of the coordination number of a chalcogen element in selenide and telluride glasses upon doping with metals has been found in other cases as well. For example, N_{Se}, the coordination number of Se in $GeSe_4$–In and $GeSe_5$–In, increases with increasing In content. In $Ge_{17}Se_{68}In_{15}$, the value is as high as 2.65 ± 0.3 [12], while the sum of N_{SeSe} and N_{SeGe}, the average number of Se and Ge atoms around Se, is close to 2, which refers to a bonding mechanism similar to that in $GaGeTe_7$. Another example is the composition $As_{34}Te_{51}Ag_{15}$, where the average coordination number of Te is as high as 3.03 ± 0.3 [13]. All these results raise the question whether the increase of the coordination number of Se and Te upon doping with metals is a more general feature.

In this paper, we present a structural investigation of $Ge_{15}Cu_x Te_{85-x}$ ($x = 5$ and 8) glasses. Glassy $Ge_{20}Te_{80}$ is also investigated as a reference system. Diffraction and EXAFS experiments are fitted simultaneously in the framework of the reverse Monte Carlo simulation technique, and short-range order parameters (coordination numbers, bond lengths) are obtained from the resulting particle configurations. According to a recent study of $Ge_{15}Cu_xTe_{85-x}$ glasses, the favourable combination of their physical properties (relatively high electrical conductivity, low heat conductivity, and high Seebeck coefficient) makes them promising thermoelectric

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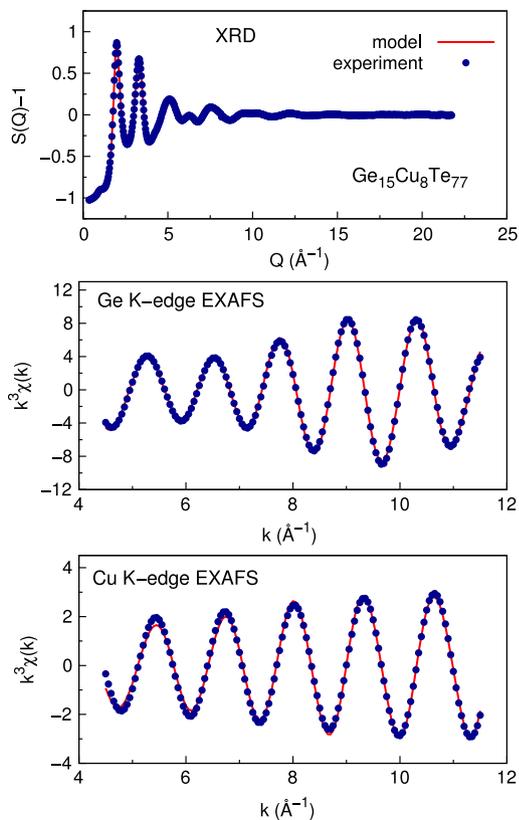
Fig. 1. Experimental X-ray diffraction (XRD) and Cu and Ge K-edge EXAFS data (symbols) of $Ge_{15}Cu_8Te_{77}$ glass compared with model curves (solid line) obtained by simultaneously fitting the three experimental datasets.

materials [14]. Thus, a detailed structural study of these glasses may be important from the point of view of applications as well.

2. Experimental

Sample preparation is described in [14]. The neutron diffraction measurement on $Ge_{20}Te_{80}$ glass was carried out at the 7C2 diffractometer (LLB, CEA-Saclay, France). The powder sample was filled into a vanadium sample holder (wall thickness 0.1 mm, diameter 6 mm). The wavelength of incident radiation was 0.72 Å. Data were normalized for monitor counts and corrected for detector efficiency, background, and incoherent scattering.

The X-ray diffraction structure factors were measured at the BW5 high-energy diffractometer [15] (HASYLAB, Hamburg, Germany). Samples were filled into quartz capillaries (wall thickness 0.02 mm, diameter 2 mm). The size of the incident beam was 2×1 mm^2. The energy of the radiation was 100.0 keV. Scattered intensities were measured by a Ge solid-state detector. Raw data were corrected for polarization, background and Compton scattering, and changes in detector solid angle.

The Cu and Ge K-edge EXAFS spectra of $Ge_{15}Cu_8Te_{77}$ and Cu K-edge EXAFS spectrum of $Ge_{15}Cu_5Te_{80}$ were measured at the Samba beamline (Soleil, France), which is installed at a bending magnet. The emitted radiation is filtered by a Pd mirror (4.5 mrad incidence, 15 keV cut-off energy) and monochromatized by a sagittal focusing Si(220) double-crystal monochromator. The Ge K-edge EXAFS measurement of $Ge_{15}Cu_5Te_8$ was carried out at beamline X of HASYLAB using a Si(111) double-crystal monochromator. Ge K-edge EXAFS spectra were recorded in transmission mode. Intensities before and after the sample position were recorded by ionization chambers filled with He–N$_2$ and Ar–He mixtures, respectively. The Cu K-edge spectra were obtained in fluorescence mode. The fluorescent intensities were measured by a Vortex

silicon drift detector. Raw data were converted to $\chi(k)$ curves using the program Viper [16].

3. Reverse Monte Carlo simulation

Simulations were carried out by using the RMC++ code [17]. The simulation boxes contained usually around 30 000 atoms. The number densities were 0.02856, 0.0300, and 0.0308 Å^{-3} for $Ge_{20}Te_{80}$, $Ge_{15}Cu_8Te_{77}$, and $Ge_{15}Cu_5Te_{80}$, respectively [18]. Test runs were carried out with configurations of 8000 atoms. The aim of these runs was to establish minimum interatomic distances. It was found that neither Ge–Ge nor Ge–Cu bonds improved the quality of the models. Either the fits did not get any better or the resulting bond distances had unrealistic values. Minimum interatomic distances were thus 3.7, 2.3, 2.5, 3.1, 2.5, and 2.3 Å for Ge–Ge, Ge–Te, Te–Te, Cu–Ge, Cu–Cu, and Cu–Te pairs, respectively. Coordination number and average coordination number constraints were also used. These will be discussed in detail later. Photoelectron backscattering factors needed to calculate the model EXAFS curves from the partial pair correlation functions [19] were obtained by using the FEFF8.4 programme [20]. Typical fit quality is shown in Fig. 1, while coordination numbers are summarized in Table 1.

4. Results and discussion

4.1. $Ge_{20}Te_{80}$

Partial pair correlation functions of $Ge_{20}Te_{80}$ obtained by simultaneously fitting X-ray diffraction, neutron diffraction, and Ge K-edge EXAFS data are shown in Fig. 2. N_{Te}, the coordination number of Te, is 2.10 ± 0.15. As this value was obtained without using constraints on Te, our result clearly indicates that the majority of Te atoms obey the $8 - N$ rule. The mean Ge–Te distance is 2.59 ± 0.02 Å, while the Te–Te bond length is 2.74 ± 0.02 Å. Both values are close to the corresponding distances found in $Ge_{15}Te_{85}$ (2.60 Å and 2.75 Å, respectively [9]), and agree well with the reported covalent radii for Ge and Te ($R_{Ge} = 1.20$–1.22 Å, $R_{Te} = 1.32$–1.38 Å [21,22]). In test runs on the $Ge_{20}Te_{80}$ composition, the average coordination number of Ge was 3.90 without using coordination constraints. As this is a clear indication that Ge is fourfold coordinated in $Ge_{20}Te_{80}$, the Ge–Te coordination number was forced to be 4 for each Ge atom in further simulations. As the Ge–Cu coordination number was below the sensitivity limit, a similar constraint ($N_{Ge} = 4$) was applied for the ternary glasses as well.

4.2. $Ge_{15}Cu_8Te_{77}$ and $Ge_{15}Cu_5Te_{80}$

During the simulation of the $Ge_{15}Cu_8Te_{77}$ glass, Ge was forced to have four Te neighbours. As has already been mentioned, Ge–Ge or Ge–Cu bonds either did not improve the fit quality or had unrealistic bond length values. For example, the mean Ge–Cu distance was 2.75 Å, which is considerably longer than the Ge–Cu distances found in different crystalline systems, such as in $Cs_8Na_{16}Cu_5Ge_{131}$ (2.35–2.48 Å) or Tm–Cu–Ge alloys (2.42–2.57 Å) [23,24], and significantly higher than the sum of the respective covalent radii, ~ 2.53 Å [21,22]. These results suggest that Ge has only Te neighbours in $Ge_{15}Cu_8Te_{77}$. The mean Ge–Te distance is 2.59 ± 0.02 Å, which agrees perfectly with the values found in glassy $Ge_{20}Te_{80}$ (2.59 ± 0.02 Å), $Ge_{15}Te_{85}$ (2.60 ± 0.02 Å) as well as in various Ge–Te-based glasses (2.60 ± 0.02 Å) [9].

Similar tests were carried out for Cu–Cu bonding, and it was found that the fit quality improved upon allowing Cu–Cu bonds. The quality of a fit is characterized by the R-factor:

$$R = \frac{\sqrt{\sum(\chi_{calc} - \chi_{exp})^2}}{\sqrt{\sum \chi_{exp}^2}}. \tag{1}$$
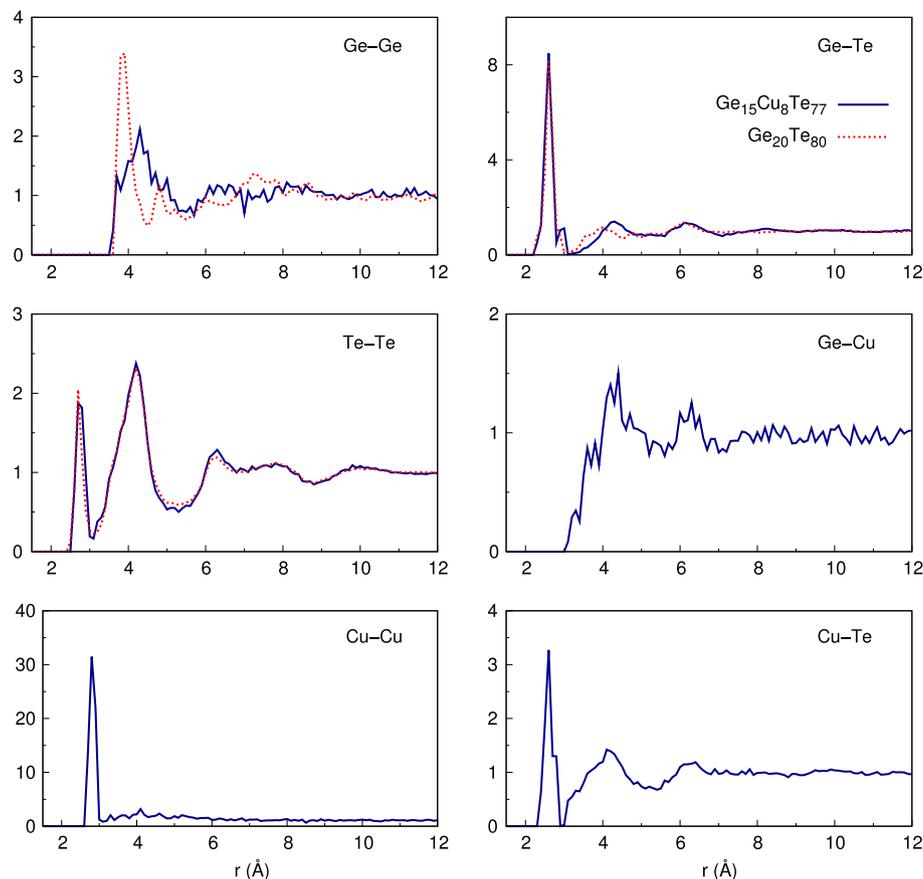
Fig. 2. Partial pair correlation functions of glassy $Ge_{20}Te_{80}$ (dots) and $Ge_{15}Cu_8Te_{77}$ (solid line).

Here, χ_{calc} and χ_{exp} are the model and experimental EXAFS curves, respectively. Elimination of Cu–Cu bonding increased the R-factor by $\sim$50% (from 6.3×10^{-3} to 9.4×10^{-3}). Partial pair correlation functions of $Ge_{15}Cu_8Te_{77}$ and $Ge_{20}Te_{80}$ are compared in Fig. 2. It can be observed that the first peak of $g_{TeTe}(r)$ shifts to higher r-values and becomes somewhat broader upon alloying with copper. It is reasonable to assume that this is a consequence of the larger variety of Te environments. In the $Ge_{20}Te_{80}$ binary glass, Te is twofold coordinated, and each Te is surrounded by Ge or Te atoms. In the $Ge_{15}Cu_8Te_{77}$ ternary glass, the coordination number of Te is 2.26 ± 0.15; thus a significant percentage of Te atoms have three neighbours. Though such details do not follow from experimental data, it can be supposed that in the case of threefold-coordinated Te atoms the strength of individual bonds decreases, implying longer bonds, which – together with the existence of shorter bonds between twofold-coordinated Te atoms – leads to the shift and broadening of the Te–Te peak. The mean Te–Te distance is 2.77 ± 0.02 Å, which is in good agreement with the Te–Te bond length (2.79–2.80 Å) found in Ge–Ga–Te glasses [9]. We note here that the weight of the Te–Te partial structure factor in the XRD total structure factor is around 75–80% in $Ge_{20}Te_{80}$ and 72–78% in $Ge_{15}Cu_8Te_{77}$. Thus XRD data are sensitive mostly to the environment of Te atoms. As the coordination number of Ge atoms was constrained in all simulations ($N_{GeTe} = 4$), the uncertainty of Te coordination number is not much higher than the usual error of average coordination numbers determined by diffraction data ($\sim$5%).

The uncertainty of N_{CuCu} and N_{CuTe} has been estimated by monitoring the R-factor while changing their values in steps of around $\pm$20–25%. It has been found that the Cu–Cu coordination number is 1.63 ± 0.8, while N_{CuTe} is about 1.73 ± 0.5. From these, the average total coordination number of Cu is estimated to be

3.4 ± 1. Generally, the coordination number of metals in chalcogenide glasses is close to this value. For example, the coordination number of Cu is 2.9 ± 0.2 in glassy $As_3Se_4Cu_2$ [25]. Indium has 3.3–3.5 neighbours in $GeSe_4$–In and $GeSe_5$–In glasses [9], while the coordination number of Ag is 3.53 ± 0.5 in $As_{34}Te_{51}Ag_{15}$ [13]. However, metal–metal bonding is either missing or less significant in these glasses.

The Cu–Cu distance in $Ge_{15}Cu_8Te_{77}$ glass was found to be 2.81 ± 0.02 Å by our simulations. As has been mentioned above, the R-factor of the Cu K-edge EXAFS data fit increased with $\sim$50% if Cu–Cu bonding was forbidden. Comparison with available literature data reveals that the Cu–Cu bond length is strongly sensitive to the environment of Cu atoms. For example, it is as short as 2.446 Å in crystalline Cu_2Te [26], while it is 2.70 ± 0.04 Å in glassy $As_3Se_4Cu_2$ [25], which is still significantly shorter than the distance found in $Ge_{15}Cu_8Te_{77}$. On the other hand, the shortest Cu–Cu distance is 2.847 ± 0.005 Å in crystalline $BaCu_2Te_2$ [27]. The mean Cu–Te distance in glassy $Ge_{15}Cu_8Te_{77}$ determined in the present work is 2.56 ± 0.02 Å, which agrees with the Cu–Te bond length in $Ge_{15}Cu_5Te_{80}$ reported by Sakurai et al. [28]. This again shows that the Cu–Cu distance is realistic in our study.

The structure of $Ge_{15}Cu_5Te_{80}$ has also been investigated with X-ray diffraction and Cu and Ge K-edge EXAFS measurements. The Cu–Cu and Cu–Te coordination numbers have also been tested for this composition. It has been found that for this composition the Cu–Cu coordination number is below the sensitivity limit ($\sim$0.3), the other coordination numbers being similar to those previously reported [28]. Thus, it can be concluded that at low concentrations (<5 at.%) Cu occupies the environment of Te and tends to avoid Ge and Cu atoms. At higher concentrations, Cu still prefers the free 'sites' around Te, but Cu–Cu bonds are also formed. This model is supported by the density data of $Ge_{15}Te_{85}$–Cu and

Table 1
Coordination numbers obtained by the reverse Monte Carlo simulation of experimental data. Coordination was constrained for values in bold.

Composition	N_{TeTe}	N_{TeGe}	N_{GeTe}	N_{CuTe}	N_{CuCu}	N_{TeCu}	N_{Te}	N_{Ge}	N_{Cu}
$Ge_{20}Te_{80}$	1.10	**1.00**	**4.02**	–	–	–	2.10	**4.02**	–
$Ge_{15}Cu_5Te_{80}$	1.25	**0.75**	**4.03**	2.37	–	0.15	2.15	**4.03**	2.37
$Ge_{15}Cu_8Te_{77}$	1.34	**0.78**	**4.00**	1.73	1.63	0.18	2.30	**4.00**	3.36

Table 2
Mass densities [18], molar volumes, and 'matrix molar volumes' (see text for details) of $Ge_{15}Te_{85}$–Cu glasses.

	x	ρ (g/cm^3)	V_{mol}(cm^3)	$V_{mol}/(100 - x)$
$Ge_{15}Te_{85}$	0	5.60	21.31	21.31
$Ge_{15}Te_{85}Cu_{2.5}$	2.44	5.72	20.63	21.14
$Ge_{15}Te_{85}Cu_5$	4.76	5.79	20.16	21.16
$Ge_{15}Te_{85}Cu_{7.5}$	6.98	5.82	19.84	21.33
$Ge_{15}Te_{85}Cu_{10}$	9.09	5.85	19.54	21.49

$Ge_{20}Te_{80}$–Cu glasses [18]. As can be seen in Table 2, the mass density of $Ge_{15}Te_{85}$–Cu glasses increases, while the molar volume decreases with increasing Cu concentration. The last column shows the molar volume of the $Ge_{15}Te_{85}$ matrix in the glass. It is defined as $V_{mol}/(100 - x)$, where V_{mol} is the molar volume of the glass and x is the Cu concentration. Thus, this quantity is the volume that contains one mole of Ge/Te atoms. It hardly depends on the composition, which shows that Cu occupies the free space of the host matrix without strongly distorting the network of Ge and Te atoms.

5. Summary

The structure of $Ge_{20}Te_{80}$, $Ge_{15}Cu_8Te_{77}$, and $Ge_{15}Cu_5Te_{80}$ glasses was investigated by diffraction techniques and extended X-ray absorption fine structure (EXAFS) measurements. Large structural models were generated by fitting experimental data by the reverse Monte Carlo simulation technique (see Table 1). In $Ge_{20}Te_{80}$ glass, both Ge and Te obey the $8-N$ rule, and the structure is built up of GeTe$_4$ tetrahedra connected via Te–Te bonding or shared Te atoms connected to two Ge atoms. The coordination number of Te is significantly higher than 2 in glassy $Ge_{15}Cu_8Te_{77}$. In $Ge_{15}Cu_5Te_{80}$ glass, Cu binds mostly to Te, while Cu–Cu bonding is significant in $Ge_{15}Cu_8Te_{77}$. Our findings show that Cu occupies the free space of the host matrix without strongly distorting the network of Ge and Te atoms.

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