Structural analysis of Cu-As-Te glasses: Results from Raman and ^{65}Cu NMR spectroscopy

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ABSTRACT

The structure of Cu-As-Te glasses is investigated using a combination of ^{65}Cu Nuclear Magnetic Resonance (NMR) and Raman spectroscopy. A comparison of ^{65}Cu NMR spectra from a series of glasses and two reference crystalline phases CuInTe_2 and CuGaTe_2 reveals that Cu in all glasses invariably adopts a tetrahedral coordination with Te. This assignment is consistent with the presence of a sharp CuTe_4 tetrahedral mode in all Cu-As-Te Raman spectra. The Raman spectra of Cu-As-Te and Ge-As-Te glasses of identical compositions suggest that the short range order of As and Te is the same in both system. ^{125}Te NMR results corroborate this hypothesis. However, the breach in chemical order commonly observed in Ge-As-Te does not appear to occur in Cu-As-Te. The variation in glass transition temperature with composition shows identical trends for Cu-As-Te and Ge-As-Te glasses, however, the density trends for these two systems show dramatic differences. Such trends are partly controlled by the difference in chemical order in these telluride glasses.

1. INTRODUCTION

Chalcogenide glasses are typically composed of elements of similar electronegativity from neighboring groups IV, V and VI on the periodic table and accordingly their structure is commonly described as amorphous networks of covalently bonded atoms where each element satisfies its valence according to the 8-N Mott rule [1]. As such, they constitute a unique category of materials with unusual electrical and optical properties that makes them critical components of many technologies ranging from non-volatile memories [2,3] to infrared optical devices [4,5]. In particular, amorphous chalcogenides are known to exhibit semiconducting properties due to their narrow band-gaps with typical E_g values of ~ 2 eV for sulfides and ~ 1.5 eV for selenides, compared to those characteristic (> 3 eV) of oxide glasses [1,6]. On the far end, telluride glasses can reach band-gap energies below 1 eV and can therefore exhibit unusually high electronic conductivities, especially when alloyed with metals such as Cu, Ag, Tl or Pb [7-12]. Within these metal-telluride systems the Cu-As-Te ternary shows one of the widest glass-formation domain and highest metal solubility [13,14]. Hence, the Cu-As-Te glasses have been investigated in the literature for various applications related to their high electrical conductivities such as phase-change memory alloys [15], electrophoretic bio-optical sensors [16,17], and more recently glassy thermoelectric materials [13,18-20].

Nevertheless, while the structure of standard tellurides from the binary As-Te and ternary Ge-As-Te systems have been extensively investigated [21-26], the structure of transition metal-arsenic-telluride glasses such as Cu-As-Te has received limited attention [27-31]. Of particular interest in this regard is the coordination environment of Cu since it is an element from group IB, which is not expected to follow the standard 8-N rule. In crystalline tellurides Cu is commonly found in tetrahedral coordination [32-34], although it is not clear whether this should be the case

in a disordered amorphous structure. So far the structure of Cu-As-Te glasses has only been investigated using diffraction techniques and analysis of total structure factors suggests a coordination number varying between 3 and 4 for Cu [28-31]. On the other hand, isotopic substitution neutron diffraction in As-Te glasses containing small amount of Cu (up to 4.8 atom%) indicates a coordination slightly larger than 4 for Cu while As and Te obey the 8-N rule [27]. In this study we apply complementary techniques including ^{65}Cu and ^{125}Te NMR and Raman spectroscopy to characterize the structure of a series of Cu-As-Te glasses with the aim of further elucidating the local coordination environment of Cu as a function of composition. The structural features are compared to those of corresponding Ge-As-Te glasses and are related to the compositional variation of their measured physical properties.

2. EXPERIMENTAL

Synthesis

Glass samples from the Cu-As-Te and Ge-As-Te system were synthesized from high purity elements (99.999% Ge and Cu, 99.99999% As, and 99.9999% Te) taken into silica ampoules previously cleaned with hydrofluoric acid and rinsed with ultra-high purity de-ionized water (18 M Ω). The silica ampoules containing the batches were then evacuated to 10^{-5} Torr and sealed under vacuum. The sealed ampoules were introduced into a rocking furnace and heated to 800-850°C for 10 h to ensure complete homogenization of the melt. The temperature of the furnace was subsequently lowered to 500-600°C for 1 h and the ampoules containing the melt were quenched in cold water. The resulting glass rods were subsequently cut and polished with alumina powder for characterization. Several series of compositions were produced

following the tie-lines depicted in Fig. 1. Powder X-ray diffraction was performed on all samples to confirm their amorphous nature (Fig. 2).

Fig. 1: Glass formation domain (shaded region) of the Cu-As-Te system (a) and Ge-As-Te system (b) showing the series of glass compositions (filled circles) synthesized in this study.

The CuInTe_2 and CuGaTe_2 crystalline phases were similarly prepared in a silica ampoule but were annealed near their melting points for 4 days to ensure complete crystallization. Both phases are characterized by a diamond-like **chalcopyrite** structure where Cu atoms belong to a CuTe_4 tetrahedral environment [33,34]. These phases were used as standards for the ^{65}Cu NMR and Raman spectroscopic measurements. The purity and the structure of the two crystalline phases were confirmed by X-Ray diffraction as depicted in Fig. 2.

Fig. 2: X-Ray diffraction patterns of a representative glass sample ($\text{Cu}_{20}\text{As}_{44}\text{Te}_{36}$) and of the two reference crystalline phases CuInTe_2 and CuGaTe_2 . Red lines immediately below the crystal diffraction patterns denote the relative intensities and positions of the main Bragg peaks for the two crystalline phases, as reported in the ICDD database (card #: 01-075-0105 and 00-006-0605 respectively).

NMR Spectroscopy

The ^{65}Cu magic-angle spinning (MAS) NMR spectra for the two crystalline compounds CuInTe_2 and CuGaTe_2 were acquired at an external magnetic field of 11.74 T (^{65}Cu resonance

frequency of 142.1 MHz) using a Bruker AQS spectrometer. Samples were crushed, packed in 4 mm ZrO₂ rotors and spun at 14.5 kHz. The ⁶⁵Cu MAS NMR spectra were obtained from Fourier transforming 4096 free induction decays collected using a solids $\pi/10$ pulse (0.45 μ s) with a 100 ms recycle delay. On the other hand, for the glass samples, the ⁶⁵Cu MAS NMR spectra were obtained at the National High Magnetic Field Laboratory, at 19.6 T (⁶⁵Cu resonance frequency of 236.2 MHz) using the previously described QMAT pulse sequence [48]. Crushed glass samples were packed into 4 mm ZrO₂ rotors and spun at 10 kHz. QMAT is a two-dimensional NMR spectroscopic technique that uses linearly varying delays between ten central-transition selective pulses to yield an “infinite spinning speed” MAS spectrum. The central-transition selective $\pi/2$ - and π -pulse lengths were 2.0 and 4.0 μ s. A total of 16 t_1 increments were employed over a single rotor period. 3200 transients were collected for each t_1 slice using a 200 ms relaxation delay between each transient allowing a full 2D spectrum to be acquired in under 3 hours. The “infinite spinning speed” MAS spectra are obtained through summation of the 16 t_1 increments after shearing and Fourier transforming both direct and indirect dimensions. All ⁶⁵Cu chemical shifts were referenced to the isotropic chemical shift of solid CuBr ($\delta_{\text{iso}} = 0$ ppm).

¹²⁵Te MAS NMR spectra were collected at 11.74T (¹²⁵Te resonance frequency of 157.7 MHz) for two glasses of composition Cu₁₀As₂₀Te₇₀ and Cu₂₀As₃₅Te₄₅. Samples were crushed and placed in a 4mm ZrO₂ rotor and spun at 14.5 kHz. The ¹²⁵Te MAS NMR spectra were obtained using a rotor-synchronized Hahn echo pulse sequence using $\pi/2$ - and π -pulse lengths of 1.9 and 3.8 μ s, respectively. Due to the low concentration of Te in the Cu₂₀As₃₅Te₄₅ sample Carr-Purcell Meiboom-Gill (CPMG) echo train acquisition was appended to the end of the sequence to increase the signal-to-noise.

Raman spectroscopy

Raman spectroscopic measurements on glassy samples were performed at ambient conditions using a Bruker RFS 100/S Fourier transform Raman spectrometer. The Raman spectrometer utilized a Nd:YAG laser operating at 1064nm and the backscattered radiation was detected using a solid state Ge detector. The power level was set to 50 mW and the resolution was 4 cm⁻¹. For the CuAsTe glasses, 8000 scans were collected and averaged to produce each Raman spectrum, while 3000 scans were collected for each of the GeAsTe glasses. Raman measurements on crystalline samples were performed using a Renishaw InVia confocal Raman spectrometer equipped with an Ar ion laser source at 514 nm at a power of 10mW with a 50X microscope objective and 200s collection time.

Differential Scanning Calorimetry

Glass transition temperature (T_g) measurements were performed using a Mettler Toledo DSC1 differential scanning calorimeter (DSC). Glass samples of mass ~5 mg were taken in sealed aluminum pan and heated well above T_g and cooled down at 10°C/min. The samples were immediately reheated at 10°C/min and the T_g was obtained from the onset of jump in heat capacity defined as the intercept of the tangent of the baseline and the heat capacity peak [13]. The DSC cell was flushed with nitrogen gas and an empty aluminum pan was used as a reference.

Density measurements

Density measurements were carried out using a Micromeritics AccuPyc II gas expansion pycnometer under a helium environment of 6N purity. Approximately 0.5–2.0 g of each sample was loaded into a 1 cm³ cup. Reported densities are averages of 10 consecutive measurements at 20 °C and are determined to within ± 0.005 g/cm³.

RESULTS:

NMR Spectroscopy:

The ⁶⁵Cu one-pulse MAS NMR spectra of the two reference crystalline phases CuInTe₂ and CuGaTe₂ are shown in Fig. 3. These spectra are characterized by a single, relatively sharp resonance with isotropic chemical shift near 500 ppm corresponding to Cu in a tetrahedral CuTe₄ environment. The presence of a strong spinning sideband pattern in the ⁶⁵Cu MAS NMR spectrum of CuInTe₂ and the lack thereof in the case of CuGaTe₂ suggest that the chemical shift anisotropy of the Cu site in the former compound is significantly larger than that in the latter.

Fig. 3: ^{65}Cu MAS NMR spectra of the two reference crystalline phases CuInTe_2 and CuGaTe_2 . Asterisks denote spinning sidebands.

The ^{65}Cu infinite-spinning-speed MAS (QMAT) NMR spectra of two series of Cu-As-Te glasses containing 10 at% Cu and 20 at% Cu are shown in Fig. 4. These spectra are all characterized by a single, relatively broad resonance with isotropic shift near 350 ppm and the line shape appears to be practically independent of glass composition. The similarity between the ^{65}Cu isotropic shifts of these spectra and those of the crystalline compounds CuInTe_2 and CuGaTe_2 suggest that Cu is likely to be tetrahedrally coordinated to four tellurium atoms in these Cu-As-Te glasses, irrespective of their chemical composition. The preference of Cu for heteropolar bonding and chemical order in telluride glasses is similar to that observed for Ge atoms in Ge-As-Te glasses where Ge is found to bond preferentially to Te even in Te-deficient glasses where this deficiency is accommodated via preferential homopolar As-As bonding [24]. However, further work is needed in future to establish the ^{65}Cu chemical shift scale for various coordination environments in crystalline tellurides before a definitive assignment of the coordination environment of Cu atoms in these glasses can be made solely on the basis of NMR results.

Fig. 4: ^{65}Cu infinite-spinning-speed MAS (QMAT) NMR spectra of Cu-As-Te glasses.

Finally, in order to investigate a potential change in Te coordination with composition, ^{125}Te MAS NMR spectra (Fig. 5) were collected on two glasses with markedly different Te concentrations ($\text{Cu}_{10}\text{As}_{20}\text{Te}_{70}$ and $\text{Cu}_{20}\text{As}_{35}\text{Te}_{45}$). The ^{125}Te MAS NMR spectra of the $\text{Cu}_{10}\text{As}_{20}\text{Te}_{70}$ glass consists of a single broad peak centered near 1000 ppm. The position of this peak shifts to ~ 200 ppm for the highly Te-deficient $\text{Cu}_{20}\text{As}_{35}\text{Te}_{45}$ glass. Such a shift in the peak position to lower frequency with increasing Te-deficiency has also been reported in the literature for GeAsTe glasses and can be ascribed to the formation of homopolar As-As bonds in the next-

nearest neighbor environment of Te atoms [47]. The chemical shift range covered by these spectral line shapes is consistent with Te being two-coordinated in these Cu-As-Te glasses [47].

Fig. 5: ^{125}Te MAS NMR spectra of two end member compositions of the Cu-As-Te series.

Raman Spectroscopy:

The Raman spectra of Cu-As-Te glasses with varying Cu content at a fixed As:Te ratio of 1:1 are shown in Fig. 6a and the spectra of corresponding compositions in the Ge-As-Te system are shown in Fig. 6b. The Raman spectra of Cu-As-Te and Ge-As-Te glasses with a fixed Cu(Ge):As ratio of 1:2 and varying Te content are shown in Figs. 6c and 6d, respectively. These unpolarized Raman spectra show three main bands near 125 cm^{-1} , 150 cm^{-1} and 185 cm^{-1} . The two lower wavenumber bands are characteristic of stretching and bending modes of AsTe_3 pyramids [23]. However, the band near 125 cm^{-1} is sharp and intense, particularly in the spectra of all Cu-As-Te glasses. Intense bands in the range $125\text{-}127\text{ cm}^{-1}$ has been previously assigned to the symmetric stretching mode of CuTe_4 tetrahedra in Cu-In-Te crystalline phases [35]. This assignment is confirmed by the Raman spectra of the reference crystalline phases CuInTe_2 and CuGaTe_2 shown in Fig. 6e and 6f which exhibit intense Raman lines in the same region. Hence a similar assignment for this band can also be made in the Raman spectra of Cu-As-Te glasses in Fig. 6a and 6c. In particular, when the As:Te ratio is kept constant, the band intensity increases consistently with Cu content (Fig. 6a). On the other hand, a band at this position is also characteristic of the ν_1 (A_1) symmetric stretching mode of the GeTe_4 tetrahedra and can be assigned as such in the Raman spectra of the Ge-As-Te glasses (Figs. 6b,d).

The Raman spectra of the Ge-As-Te glasses are consistent with those reported in the literature for similar glasses [23,36,37] and they show similar features as those characteristic of the Cu-As-Te glasses. An interesting point to note is that the band in the Raman spectra of Ge-As-Te glasses near 150 cm^{-1} splits and a new band appears near 145 cm^{-1} and grows with increasing Ge content. This band therefore is likely associated with Ge-Te stretches. Finally, a band near 185 cm^{-1} grows with decreasing Te content and is present in the Raman spectra of all

Te-deficient glasses. This band may be assigned to Ge-As or As-As vibrations and is present even in the Raman spectrum of the Ge-As-Te glass (Fig. 7d) with the highest Te concentration [23]. It is indeed well established that chemical order is violated in Ge-As-Te glasses and that a significant fraction of As-As bonds is present, even in Te-excess glasses [24,26]. In contrast, this band is practically absent in the Cu-As-Te glass with the highest Te concentration (Fig. 6c) suggesting that these glasses are likely more chemically ordered than their Ge-As-Te counterparts.

Fig. 6: Raman spectra of CuAsTe (a,c) and GeAsTe (b,d) glasses with fixed As:Te ratio 1:1 (a,b) and fixed Cu(Ge):As ratio 1:2 (c,d). (a, b, c, d) spectra are arbitrarily normalized to the

intensity of the band near 150 cm^{-1} . Signal near 85 cm^{-1} denoted by an asterisk is from the **aluminum** sample holder. (e, f) are spectra of the crystalline reference samples CuInTe_2 and CuGaTe_2 respectively.

Table 1: Physical properties and average coordination number of CuAsTe and GeAsTe synthesized in this study.

Cu%	Ge%	As%	Te%	$\langle r \rangle$	T_g ($^{\circ}\text{C}$)	ρ (g/cm^3)	V_m (cm^3/mol)
20		20	60	2.6	128	-	-
20		35	45	2.75	163	-	-
20		40	40	2.8	173	5.949	15.752
20		44	36	2.84	183	-	-
15		15	70	2.45	106	-	-
15		30	55	2.6	133	5.958	17.150
15		42.5	42.5	2.725	161	5.871	16.283
15		46.75	38.25	2.766	175	-	-
10		20	70	2.4	102	5.955	18.581
10		40	50	2.6	140	-	-
10		45	45	2.65	148	5.745	16.968
10		49.5	40.5	2.695	157	-	-
5		47.5	47.5	2.575	137	5.631	17.646
5		52.25	42.75	2.622	150	-	-
	20	40	40	2.8	236	5.298	18.032
	15	15	70	2.45	149	-	-
	15	30	55	2.6	178	5.447	19.001
	15	42.5	42.5	2.725	203	5.337	18.169
	10	20	70	2.4	130	5.576	20.010
	10	45	45	2.65	170	5.497	17.901
	5	47.5	47.5	2.575	150	5.486	18.198

Glass Transition Temperature:

Due to the well-defined covalent bonding of their component elements that often strictly follow the 8-N coordination rule, chalcogenide glasses are often discussed in terms of the average number of bonds per atoms quantified by the mean coordination number $\langle r \rangle$, a measure of the

average connectivity of the atomic structure [38] (Table 1). The glass transition temperature of chalcogenide glasses is usually found to correlate closely to $\langle r \rangle$, especially in ternary systems, due to the increasing thermal energy required to break higher bond densities [39-41]. The dependence of the glass transition temperature T_g upon $\langle r \rangle$ is shown in Fig. 7 for the Ge-As-Te and Cu-As-Te systems. For the Cu-As-Te system, the average coordination $\langle r \rangle$ is calculated by assuming a coordination of 4 for Cu, as evidenced by the ^{65}Cu NMR results. An almost linear dependence of T_g upon $\langle r \rangle$ is found, similar to that of the Ge-As-Se system [40], but the average T_g values are lower for Cu containing glasses than Ge glasses. This observation is consistent with the significantly lower energy of the Cu-Te bonds (230 kJ/mol) relative to that of the Ge-Te bonds (396 kJ/mol) [42]. Nevertheless the dependence of T_g upon $\langle r \rangle$ shows an analogous linear trend for both systems which suggest that Cu and Ge contribute similarly to $\langle r \rangle$. This further supports the 4-coordinated nature of Cu atoms.

Fig. 7: Glass transition temperatures for series of samples from the Cu-As-Te (black squares) and Ge-As-Te (red dots) systems.

Density and Molar Volume:

While the Raman spectra and glass transition temperatures of Cu-As-Te and Ge-As-Te glasses shows marked similarity, the density and molar volume of the two glass families exhibit notable differences. Although the molar volumes of glasses with fixed Cu:As ratio behave the same as those with fixed Ge:As ratio and in both cases molar volume increases with increasing Te content (Fig. 8a); the molar volume of Cu-As-Te glasses with constant As/Te ratio decreases linearly with Cu content while that of Ge glasses remain constant (Fig. 8b). This suggests a

fundamental difference in the contribution of Cu and Ge atoms to the structural packing of arsenic telluride glasses.

a)

b)

Fig. 8: (a) Density (left) and molar volume (right) of glasses with fixed Cu:As (black squares) or Ge:As (red dots) ratio (1:2) and increasing Te content. (b) Density (left) and molar volume (right) of glasses with fixed As:Te ratio of 1:1 and increasing Cu (black squares) or Ge (red dots) Note: Error bars are within the size of the symbols.

DISCUSSION

Due to the large quadrupolar coupling constants, Cu NMR spectroscopy is experimentally challenging and has rarely been applied to the structural study of amorphous solids [43]. However, the present results show that ^{65}Cu NMR spectroscopy can be an effective probe of Cu environment in telluride glasses. In particular the ^{65}Cu NMR spectra of the Cu-As-Te glasses are consistent with the chemical shifts derived from crystalline reference samples which indicate a fourfold coordination for Cu in all glasses with Cu forming CuTe_4 tetrahedra in the structural network. The presence of CuTe_4 tetrahedra in Cu-As-Te glasses is also consistent with the Raman spectra which exhibit a characteristic tetrahedral CuTe_4 stretching mode at 125 cm^{-1} . Finally, the 4-fold coordination of Cu is also consistent with the evolution of T_g with average coordination $\langle r \rangle$ which mimics that of the corresponding glasses in the Ge-As-Te system where the 4-fold symmetry of Ge is unambiguous.

The observation of the same As-Te network modes in the Raman spectra of Cu-As-Te and Ge-As-Te glasses suggests that the short range order of the As-Te network is similar and hence, it is expected that Te and As atoms follow the 8–N rule of coordination for all compositions. This hypothesis is indeed consistent with the ^{125}Te NMR spectra which exhibit chemical shifts characteristic of Te atoms in twofold coordination for compositions at both ends of the glass-formation domain. This result is also consistent with previously reported neutron diffraction data which suggested that addition of Cu to As-Te base glasses had little effect on the host atoms coordination [27].

In spite of these similarities between the coordination environments of constituent atoms in Cu-As-Te and Ge-As-Te glasses, compositional evolution of density or molar volume clearly

show interesting differences between these two systems. The molar volumes of glasses with fixed Cu:As or Ge:As ratio increase with increasing Te content (Fig. 8a). This trend can be explained when one considers that addition of Te results in the formation of Te-Te chain segments with poor packing that dominates the molar volume behavior, **in addition to the larger radius of Te**. However, for glasses with As:Te = 1:1, addition of Cu results in rapid increase in density (decrease in molar volume) while addition of Ge decreases the density (insignificant change in molar volume) for equivalent compositions. This behavior for the Cu-As-Te glasses can be ascribed to increasing atomic packing due to an increase in the average coordination number as fourfold coordinated Cu replaces threefold coordinated As and twofold coordinated Te in the glass structure. Considering the **tetrahedral** coordination of Cu and Ge and their preference for bonding with Te, one would expect an identical molar volume scenario for the corresponding Ge-As-Te glasses, however, Fig. 8b shows that this is not the case. This difference in behavior can be ascribed to the well-established breach of chemical order observed in Ge-As-Te glasses which does not appear to occur in Cu-As-Te glasses. Indeed, the Raman spectra of Ge-As-Te glasses show the presence of homopolar As-As bonds (peak at 185 cm^{-1}) even in Te-rich glasses (Figs. 6b,d) while this mode is only present in Te-deficient glasses for the Cu-As-Te samples (Fig. 6a,c). The presence of these As-As bonds may affect the molar volume in two ways: (i) An increase in As-As bond concentration must be compensated by an increasing concentration of poorly packed Te-Te segments which raise the molar volume; (ii) It was suggested in the literature that the formation of As-As bonds in As-Se glasses produces quasi-linear $\text{Se}_2\text{As-AsSe}_2$ fragments which lowers structural packing and glass density [44]. Similar $\text{Te}_2\text{As-AsTe}_2$ fragments may also be present in Te-deficient Cu-As-Te and Ge-As-Te glasses. Therefore, the increase in molar volume due to the formation of homopolar As-As bonds can

offset the decrease in molar volume due to the formation of GeTe_4 tetrahedra and offer a possible explanation for the constant molar volume of Ge-As-Te glasses observed in Fig. 8d.

CONCLUSION

A combination of ^{65}Cu NMR and Raman spectroscopy is utilized to the structural investigation of Cu-As-Te glasses. The results indicate the presence of Cu predominantly in tetrahedral CuTe_4 environments in all glasses. The Raman modes of Cu-As-Te and Ge-As-Te glasses suggest that the coordination numbers of Te and As follow the 8-N rule for all compositions but indicate that the breach of chemical order well-known in Ge-As-Te does not occur in Cu-As-Te. The change in T_g with average coordination shows a similar variation between the Cu-As-Te and Ge-As-Te glasses of the same stoichiometry, supporting the tetrahedral coordination of Cu, identical to that of Ge. Nevertheless, glasses in these two systems show important differences in the compositional variation of density as a function of Cu or Ge content at constant As:Te ratios that can be partially attributed to the corresponding differences in the relative degrees of chemical order in these two systems.

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