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Origin of high thermal stability of amorphous Ge₁Cu₂Te₃ alloy: A significant Cu-bonding reconfiguration modulated by Te lone-pair electrons for crystallization

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Abstract— $Ge_1Cu_2Te_3$ is an important candidate for high-temperature phase change memory due to the fine amorphous stability. Yet, the basic bonding chemistry for its high-temperature application is still not completely clear. In this work, a new bonding mechanism for its amorphous and crystalline phases is proposed and demonstrated by first-principles calculations. Compared to the tetrahedral environment distributed evenly in crystalline form, Cu atoms in the amorphous state tend to be accumulated as trigonal clusters. For the crystalline phase, a bonding configuration of nonequivalent sp^3 hybridization with Te lone-pair electrons is proposed without Cu *d* electron participation. In the amorphous phase, however, a significant bonding reconfiguration of Cu *d* electrons occurs due to the isolation of the Te lone-pair electrons. Therefore, the notable contrast in the Cu atomic and electronic structures between the crystalline and amorphous phases results in an obvious phase transition barrier for high-temperature storage. The mechanism presented in this study serves as a reference for other transition-metal alloyed phase-change materials. © 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: Bonding chemistry/physics; Thermodynamic stability; Phase transition; First-principles calculations

1. Introduction

Phase change memory (PCM) is a promising technique for next-generation non-volatile data storage [1–4]. Such data storage devices depend mainly on PCM materials, which have reversible phase transitions and maintain significant signal contrast. The phase transition can be triggered by an electrical pulse or laser pulse [5]. As the most popular PCM material, $Ge_2Sb_2Te_5$ (GST) has been used for commercial applications in rewritable digital versatile disc-random access memory (DVD-RAM) and Blu-ray disc rewritable (BD-RE) [6]. However, the 10 year-lifetime temperature of GST is just 85 °C [7], which is well below the standard of international technology roadmap for semiconductors (125 °C for phase change random access memory (PCRAM) in 2013). Therefore, its poor amorphous stability makes GST unsuitable in high-temperature applications such as automotive PCM.

In 2012, Sutou et al. [8] reported that Ge₁Cu₂Te₃ (GCT) possesses an exceptional amorphous thermal stability; the operating temperature for 10 year data retention can reach 130 °C, making GCT a suitable candidate for high-temperature PCM applications. In 2013, Saito et al. [9] reported that GCT shows larger optical reflectance in the amorphous state than in the crystal state, which is markedly different from the behavior of prevailing PCM materials. Recently, Skelton et al. [10] carried out first-principles calculations to explore the unusual optical contrast between the two GCT states. They considered the resonant bonding [11], which is necessary for high reflectance, may be suppressed in the crystal. Yet, the physical origin of the stability of amorphous Ge₁Cu₂Te₃ (a-GCT) remains not very clear, hindering further material optimization and exploration of PCM applications. Thus, understanding the detailed bonding mechanism will be helpful to comprehend the origin of the stability property or even to develop new similar materials.

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In this work, we employ ab initio molecular dynamics (AIMD) [12] to investigate the basic bonding rule of GCT. The origins of the thermal stability are analyzed in terms of atomic and electronic structures by comparing the structures of GCT and GST. In GST, the atomic structures of the crystalline and amorphous states are similar; both possess local octahedral 4-fold rings [13]. In contrast, GCT has large differences in local structure between its crystalline and amorphous phases; particularly the Cu-participant triangle clusters are only found in the amorphous state. This large difference naturally makes the phase-transition difficult, resulting in enhanced thermal stability. A mechanism of bonding reconfiguration between sp^{3} -hybridized crystalline Ge₁Cu₂Te₃ (c-GCT) and d electron-participated a-GCT is demonstrated, which is in contrast to the main p bonding in both states of GST. This reconfiguration from a-GCT to c-GCT requires a significant modulation of the Te lone-pair electrons. The mechanism can serve as a reference for other transitionmetal alloyed/doped PCM materials.

2. Simulation methods

The study employs density functional theory (DFT) with the generalized gradient approximation (GGA) [14] and projected augmented plane waves (PAW) pseudopotential [15] as implemented in the VASP code [16,17]. We employ a 90 atom cubic supercell including 15 Ge atoms, 30 Cu atoms, and 45 Te atoms to mimic Ge1Cu2Te3 with an experimental amorphous density of 6.06 g/cm³ [9]. The amorphous model is realized by the melt-quenching technique as described in Fig. S1 of Supplementary material. First, atoms are randomly filled according to the experimental amorphous density. The atoms are then diffused at 3000 K using AIMD for 6 ps to eliminate the initial setup memory. To obtain a reasonable liquid, a 9 ps MD simulation at 1000 K (close to the melting point) is run. Subsequently, the melt is quenched directly to 300 K and maintained for another 9 ps. The last 1000 frames at 300 K are averaged for the structural analysis. To calculate electronic character, the final amorphous structure from AIMD is locally relaxed for better static balance position. A unit cell of the GCT crystal model [18] is analyzed for comparison. The AIMD timestep is 3 fs, and the energy cutoff is 355 eV. For a-GCT, the K-points for MD and static self-consistent calculations are $1 \times 1 \times 1$ and $3 \times 3 \times 3$ Monkhorst-Pack mesh, respectively. For c-GCT, the K-points for relaxation and property calculation are $2 \times 6 \times 4$ and $4 \times 12 \times 8$, respectively.

3. Results and discussion

To check the reasonableness of the present a-GCT model, we first calculate the X-ray structure factor and compare that with an experiment (Fig. S2 in Supplementary material). The results are in good agreement. Then the optical reflectance is also calculated. In Fig. S3 of Supplementary material, the simulated reflectance of a-GCT is higher than that of c-GCT, which is consistent with the experiment [8]. Such an optical contrast is just opposite to that in many other PCM materials; thus, this feature makes GCT unique among PCM materials. We also perform crystallization AIMD to directly verify the thermal stability of a-GCT. For comparison, an amorphous GST (a-GST) model (87 atoms + 9 vacancies) is obtained, and its crystallization is also carried out. After 180 ps at 600 K, a-GST is at least partial crystallized, while a-GCT shows no sign of crystallization in Fig. 1. This behavior is also demonstrated by the free-energy evolution. Generally, the drop of free energy with time strongly indicates crystallization happens. It is very clear that the free energy of GST always decreases with time while that of GCT almost remains the same. Thus, the present GCT model in our calculation is physically reasonable and can be used to analyze the bonding rules.

Next, we try to summarize the atomic chemical environment in GCT. The pair correlation function (PCF) is useful in analyzing the local structure of the amorphous state [19]. Fig. S4 of Supplementary material separates all the atomic pair correlations to see the bonding tendency in a-GCT. The convergence of the PCFs to 1 at a large distance demonstrates the complete disorder of the present model. By the way, the considerable homopolar Cu–Cu and Ge– Ge bonds reveal the intense chemical disorder.

In Table 1, the average coordination number (CN) for all elements is 4.36; this value is close to the CN of 4.07 reported from reverse Monte Carlo (RMC) simulation [20]. The present CN differs from previous works [10] due to the different cutoff selections (see Supplementary material); however, the overall trend is consistent. Notably, in this



Fig. 1. Structural snapshots before and after a 180 ps crystallization AIMD at 600 K for GCT (a) and GST (b). The corresponding evolutions of their relative free energies from the MD are compared in (c).

N_{Ge} N_{Cu} N_{Te} $N_{\rm tot}$ N_{tot(RMC)} Around Ge 0.377 (0.025) 0.578 (0.019) 2.729 (0.061) 3.684 4.03 Around Cu 0.289 (0.019) 1.860 (0.062) 3.602 (0.080) 5.751 4.06 0.910 (0.061) 2.401 (0.080) 0.348 (0.008) 4.10 Around Te 3.659

Table 1. The total and partial coordination numbers (CN). The total CN from RMC is also listed. The normalized coordination number (NCN) defined in the Supplementary material is shown in parentheses.

^a Jovari et al. (Ref. [20]).

study, Cu has a max CN close to 6, while Ge and Te have smaller CNs than those from the RMC study [20]. Here, the high CN of Cu may result from its metallic characteristics as it forms Cu–Cu bonds in addition to covalent Cu–Ge or Cu–Te bonds. To identify the intrinsic bonding ability, we normalize the CN of the center element by the number of its surrounding element (NCN, see Supplementary material). From the NCN values (Table 1, in parentheses), we infer that the bonding tendency in a-GCT follows the sequence (from strong to weak): Cu–Te/Te–Cu, Cu–Cu, Ge–Te/Te–Ge, Ge–Ge, Ge–Cu/Cu–Ge, and Te–Te.

Bond angle distributions (BADs) are useful to detect local structural features [19]. For example, a 109.5° angle indicates a sp^3 -hybridized tetrahedral motif, while 90° often implies a p-bonding octahedral motif. Fig. 2 shows the BAD centered at every element and separated with different neighbors. It is noted that c-GCT has a tetrahedral local environment [18], while crystalline GST (c-GST) possesses an octahedral one. This can be explained by the average number of valence electrons, which is different between tetrahedral (<4.25) and octahedral (>4.25) crystal structures [21]. In a-GCT, Ge, Cu, and Te have broad BAD peaks at 100°, 105°, and 107°, respectively. These main BADs are close to those of a tetrahedral structure (109.5°). However, the striking contrast is indicated by an obvious BAD peaking at 60°. We decompose the BAD into different connections to identify the origin of this peak. First, almost none of the Ge-center BAD has an obvious 60° distribution (Fig. 2(a)), indicating that Ge retains its

 sp^3 bonding. Second, the BAD of 60° requires Cu-related bonds such as Cu–Cu and Cu–Te (Fig. 2(b)–(c)). We then highlight the Cu-related bonding in Fig. S5(a) and observe a considerable amount of 3-fold rings, directly showing the special 60° BAD. Third, the connected 3-fold rings form cage-like triangular clusters, implying a certain degree of Cu accumulation. Therefore, in the presence of Cu, GCT has a significant structural contrast between its amorphous and crystalline states. The structural characteristics discussed above (including PCF, CN, and BAD) are consistent with previous published models [10]. This is further evidence in support of our amorphous GCT model.

While the BAD can identify the local structures, the ring distributions in amorphous materials often give the intermediate range order information. The ring distribution statistics for the amorphous and crystal GCT was calculated up to 8-fold ring, as shown in Fig. 2(d). The amorphous GCT is dominated by 3/5/7-fold rings while the crystal GCT is only composed of 6-fold rings. The big contrast implied that the reconstruction in the crystallization process must be very significant. On the other hand, in the case of GST, the amorphous structure is dominated by 4-fold and 6-fold rings which is just analogous to the crystal phase [13,22]. In addition, as the 3-fold rings are dominant in a-GCT but missing in c-GCT, the decreasing of 3-fold rings during crystallization can also be used to estimate the crystallization degree. The simulation (Fig. S5(b) in Supplementary material) results suggest that the amorphous GCT is very stable.



Fig. 2. The bond angle distributions (BADs) and ring distributions in a-Ge₁Cu₂Te₃. (a)–(c) The partial BADs around Ge, Te, and Cu atoms, respectively. The symbol X can be any type of atom; for example, Ge–Ge–X indicates the bond angle of a Ge atom with at least one bonded Ge. (d) The ring distributions in amorphous structure. The inset is the ring distribution in its crystal for comparison.

In Fig. 3, we summarize the local structural motifs of GCT and GST to understand their amorphous stabilities. With the exception of the 33% of Ge atoms that have local tetrahedral environments, most of the motifs in a-GST are composed of 4-fold rings [23,24]. The large amount of 4-fold rings in both states of GST indicates a similar local octahedral environment (Fig. 3(a)). Thus, crystallization is realized by the rotation of these rings without breaking too many chemical bonds. In contrast, GCT shows completely different local structures around Cu between its two states (Fig. 3(b)). In the amorphous model, approximately 93%of the Cu atoms from the original tetrahedral motif in the crystalline state are involved in the 3-fold rings. This proportion is far greater than that of tetrahedral Ge in amorphous GST. Thus, large amounts of chemical bonds must be broken and reformed during crystallization. In addition, Cu atoms are gathered in clusters, thus Cu diffusion is necessary during the phase transition.

Atomic chemical environment is a premise to understand the basic roles of bonding chemistry. For example, the atomic similarity of the two states in GST comes from their similar p-orbital electronic characters. As such, the large contrast in atomic structure between the two states of GCT must indicate their considerably different bonding characteristics. To gain the insightful origins of the thermal stability of a-GCT, electronic structures are investigated below in detail.

In c-GCT, a charge density difference (CDD) [25] shows an electron pileup between atoms, indicating typical covalent bonding (Fig. 4(a)). From the average valence electron number and the local tetrahedral environment, we can easily infer that c-GCT satisfies sp^3 hybridization behavior. From this information, the electronic structures are proposed in Fig. 4(b) and (c). Although Cu and Te do not have just four valence electrons like Ge, they can achieve sp^3 configuration through nonequivalent hybridizations. A part of the Cu–Te (see Cu–Te-2 in Fig. 4(c)) bonding orbital can then be filled by lone-pair electrons of Te without Cu electrons. In other words, Te supplies redundant electrons to the system to compensate for the Cu electron deficiency.

We note that this nonequivalent sp^3 hybridization in Te atoms is similar to the case of oxygen atom hybridization in H₂O molecules [26]. This finding is a striking contrast to the *p*-orbital bonding of Te atoms in conventional PCM



Fig. 3. Schematic of the atomic structure comparison between the amorphous and crystalline phases of (a) GST and (b) GCT. All the motifs are from the simulated models described above.



Fig. 4. Bonding chemistry of c-GCT. (a) The 3D display of CDD isosurfaces with 0.007 e/a_0^3 ($a_0 = \text{Bohr}$). The yellow areas indicate the increases in charge density, while the blue areas represent the decreases in charge density. (b) Schematic of atomic orbitals of nonequivalent sp^3 hybridization. (c) Schematic of bonding orbitals. The arrows are electrons while the circles are orbitals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

materials. Interestingly, the Cu–Te bonding by the Te lone-pair electrons is somewhat similar to the dative Ge–Te bonding with Te lone-pair electrons in GST and the GeTe alloy [27,28].

In the case of a-GCT, the bonding configuration above is destroyed, as reflected in the significant changes in BAD. Although the bonds remain mainly covalent in character with the exception of the metallic Cu-Cu bond (Fig. 5(a)-(e)), the electron localization function (ELF) indicates obvious lone-pair electrons isolated around Te atoms (Fig. 5(f)). In fact, the increase in the total average CN in a-GCT suggests more electrons are required in bonding compared to in c-GCT. However, when we consider the whole system, electrons are deficient because Te retrieves its electrons from an original bond to form its lone pair. To make up for these lacking electrons, the only source is the d electrons of Cu. Indeed, the distribution of d electrons in a-GCT in the partial density of state (PDOS; Fig. 5(g)) is broader than that in c-GCT, indicating that d electrons are involved in bonding.

To further identify the role of Cu d electrons, we compare the d electron distribution between the crystal and amorphous phases (Fig. 6). The narrow energy window from -2.56 eV to -2.36 eV is selected to contain the location of Cu d electrons (the shadowed regions of the PDOS in Fig. 6(a) and (c)). Thus, the distribution in real space can identify the role of d electrons. In c-GCT, the d electrons are localized only around Cu atoms and are not involved in external bonding (Fig. 6(b)). The shapes of the electron clouds are similar to those of d orbitals. This non-bonding characteristic of d electrons is direct evidence for the proposed electronic model of crystalline GCT in Fig. 4. In contrast, the *d* electron clouds in a-GCT are quite delocalized (Fig. 6(d)). The significant electron distribution is observed to link Cu-Cu atoms. In other words, the d electrons of Cu come out to form direct bonds in the amorphous state. This d electron bonding is also demonstrated in bulk Cu metal (see the broad distributions in the PDOS of Fig. 5(g)), whose atoms are close-packed with a BAD of 60°. In fact,



Fig. 5. Bonding chemistry of a-GCT. (a) The 3D display of CDD isosurfaces with 0.007 e/a_0^3 ($a_0 = bohr$). The yellow areas indicate the increases in charge density while the blue areas represent the decreases in charge density. (b)–(e) Slices with the graded distribution of CDD along bonds. (f) The 3D display of 0.9 ELF isosurfaces. The yellow 'little hat' in the opposite direction of bonding indicates lone-pair electrons. (g) The PDOS of Cu elements in different chemical environment including a-GCT, c-GCT and pure Cu metal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 6. The partial density of states (PDOS) of c-GCT (a) and a-GCT (c). The partial charge density distribution for Cu *d* electrons of c-GCT (b) and a-GCT (d) in the specific energy window of -2.56 to -2.36 eV, indicated as the shadowed regions in PDOS. The isosurface is 0.0015 e/ a_0^3 ($a_0 = Bohr$).

we can understand that these retrieved Te lone pairs make Cu *d* electrons bonding and forming 3-fold rings. In GST, the *p*-bonding characteristic is not significantly altered [28]. Therefore, the bonding reconfiguration of GCT between Cu *d* electrons and Te lone-pair electrons plays a critical role in amorphous stability. As a metaphor, the reconfigured bonding of Cu *d* electrons is the lock to stabilize the amorphous phase through triangular clusters, and the Te lone pair is the unlocking key to switch the behavior of Cu d electrons.

4. Conclusions

In summary, we investigate the bonding chemistry of the GCT alloy through first-principles calculations. a-GCT shows a significant chemical disorder with large amounts of homopolar bonds. Cage-like triangular clusters composed of 3-fold rings are related to the Cu atoms. The bonding mechanism in c-GCT is proposed and demonstrated by the nonequivalent sp^3 hybridization with Te lone-pair electrons. In contrast, a-GCT requires Cu *d* electrons to participate in bonding due to the isolation of the Te lone pair. Thus, the vast difference in atomic and electronic structures between a-GCT and c-GCT leads to the high amorphous stability for its perfect data retention. This mechanism may act as a reference for other transition metal alloyed PCM materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.actamat.2015.02.015.

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