Structural basis for the fast phase change of Ge2Sb2Te5: Ring statistics analogy between the crystal and amorphous states

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Structural basis for the fast phase change of Ge$_2$Sb$_2$Te$_5$: Ring statistics analogy between the crystal and amorphous states

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The three-dimensional atomic configuration of amorphous Ge$_2$Sb$_2$Te$_5$ and GeTe were derived by reverse Monte Carlo simulation with synchrotron-radiation x-ray diffraction data. The authors found that amorphous Ge$_2$Sb$_2$Te$_5$ can be regarded as “even-numbered ring structure,” because the ring statistics is dominated by four- and six-fold rings analogous to the crystal phase. On the other hand, the formation of Ge–Ge homopolar bonds in amorphous GeTe constructs both odd- and even-numbered rings. They believe that the unusual ring statistics of amorphous Ge$_2$Sb$_2$Te$_5$ is the key for the fast crystallization speed of the material. © 2006 American Institute of Physics.

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The development of fast phase-change materials in the last century was accomplished by the landmark studies of Chen et al. on GeTe compound and Yamada et al. on Au–Ge–Sn–Te in a single-phase structure. They reported that these materials show a high-phase stability of the amorphous phase and a very short crystallization time. The pseudobinary system, and GeTe exhibits trigonal-type structure with 20% vacancy of Ge/Sb mixing site due to the formation of Ge–Ge homopolar bonds in amorphous GeTe constructs both odd- and even-numbered rings. Therefore we derived the large-scale atomic structures of a-Ge$_2$Sb$_2$Te$_5$ and a-GeTe using reverse Monte Carlo (RMC) simulation on the high-energy synchrotron x-ray diffraction.

In this letter, we focused on amorphous Ge$_2$Sb$_2$Te$_5$ (a-Ge$_2$Sb$_2$Te$_5$) (crystallization speed: 20 ns) and GeTe (a-GeTe), crystallization speed: 100 ns) to understand the relationship between the atomic structure and the speed of phase change in DVD-RAM. The crystal structures of these materials are reported that Ge$_2$Sb$_2$Te$_5$ exhibits NaCl-type structure with 20% vacancy of Ge/Sb mixing site due to the density change. On the other hand, the structure of the amorphous phase in both materials is still unknown. However, small density (volume) change due to the large amount of vacancy in the crystal phase during the crystallization of the amorphous phase in Ge$_2$Sb$_2$Te$_5$ suggests that a-Ge$_2$Sb$_2$Te$_5$ exhibits a unique amorphous structure. Therefore we derived the large-scale atomic structures of a-Ge$_2$Sb$_2$Te$_5$ and a-GeTe using reverse Monte Carlo (RMC) simulation on the high-energy synchrotron x-ray diffraction.

The detail of preparation of the Ge$_2$Sb$_2$Te$_5$ and GeTe specimens is described elsewhere. The high-energy x-ray diffraction experiments were carried out at the SPring-8 beamline BL02B2 (Ref. 13) and BL04B2. The details of data analysis are described elsewhere. The RMC simulation was performed on an ensemble of 3686 and 4096 particles for Ge$_2$Sb$_2$Te$_5$ and GeTe, respectively, starting with the...
the diffraction patterns of Ge$_2$Sb$_2$Te$_5$ consist of sharp Bragg reflections, indicating the long-range structural resemblances that cause the fast phase change. However, there must be some hidden between the amorphous and crystal phases for giving an insight not make us realize a remarkable structural resemblance between.

Partial-pair distribution functions. The atomic number density of the amorphous phase.

Figure 1(a) shows the measured structure factors $S(Q)$. The diffraction pattern of Ge$_2$Sb$_2$Te$_5$ and GeTe crystals consists of sharp Bragg reflections, indicating the long-range periodicity in the atomic arrangement. On the other hand, the diffraction patterns of Ge$_2$Sb$_2$Te$_5$ (953 K) and GeTe (1073 K) liquids show a typical halo pattern peculiar to non-crystalline materials, reflecting the lack of the long-range periodicity. These diffraction patterns show that both Ge$_2$Sb$_2$Te$_5$ and GeTe have to undergo such a highly disordered state (liquid state) during a recording process (crystal-amorphous phase change) by a laser-heated melt-quench process. Figure 1(b) shows total correlation functions $T(r)$ derived by the Fourier transformation of $S(Q)$. The first peak observed at around 3.0 Å in the $T(r)$ of both crystals is assigned to the Ge(Sb)–Te bonds. One may notice the shrinkage of the Ge(Sb)–Te bond distance at the phase change from the crystal to the amorphous phase. The variation of the atomic distance and peak height can be ascribed to the reduction of the coordination number of the Te atom around the Ge(Sb) atom. Unfortunately the comparison among the crystal, liquid, and amorphous Ge$_2$Sb$_2$Te$_5$ and GeTe data can not make us realize a remarkable structural resemblance between the amorphous and crystal phases for giving an insight of fast phase change. However, there must be some hidden structural resemblances that cause the fast phase change between the crystal and amorphous structures.

The total structure factors $S(Q)$ of $a$-Ge$_2$Sb$_2$Te$_5$ and $a$-GeTe derived from the RMC model are shown in Fig. 1(a) as a red line. It is confirmed that the RMC models are consistent with experimental data. It is worth mentioning that partial-pair distribution functions $g_{ij}(r)$ of Ge–Te and Sb–Te [Fig. S1 in EPAPS (Ref. 17)] derived from the RMC model are sharp but skewed towards the high-$r$ side, indicating a distribution of the Ge–Te and Sb–Te distances from 2.4 to 3.4 Å due to highly distorted structural units. Furthermore, the formation of Ge–Ge homopolar bond in $a$-GeTe is confirmed in $g_{ij}(r)$ of Ge–Ge, whereas the formation of Ge(Sb)–Ge(Sb) bonds in $a$-Ge$_2$Sb$_2$Te$_5$ is not confirmed from our RMC simulations. In order to characterize the structural units, we investigated the bond angle distributions within the first coordination shell of the $g_{ij}(r)$ [Fig. S2 in EPAPS (Ref. 17)]. Te–Ge(Sb)–Te and Ge(Sb)–Te–Ge(Sb) in $a$-Ge$_2$Sb$_2$Te$_5$ exhibit a peak at around 90°, which surprisingly consist with the angle in the corresponding crystal phase and are different from the typical bond angle, 109.4°, of the O–Si–O of regular tetrahedra, SiO$_4$, in amorphous SiO$_2$. Te–Ge–Te in $a$-GeTe exhibits similar bond angle distribution, but Ge–Te–Ge shows peaks at around 90° and 50° due to the formation of Ge–Ge homopolar bond. Therefore it is suggested that $a$-Ge$_2$Sb$_2$Te$_5$ possesses a crystal-like bond angle order, whereas $a$-GeTe loses such an order by the formation of Ge–Ge bond. The total coordination number around the Ge(Sb) derived from the RMC model [Table SI in EPAPS (Ref. 17)] is estimated at 3.7 (3.0) for $a$-Ge$_2$Sb$_2$Te$_5$ and around the Ge is 4.1 for $a$-GeTe. Therefore it is suggested that dominant short-range structural units are GeTe$_4$ and SbTe$_3$ for $a$-Ge$_2$Sb$_2$Te$_5$, and GeTe$_4$ and GeTe$_2$Ge for $a$-GeTe.

The ring statistics for the amorphous and crystal Ge$_2$Sb$_2$Te$_5$ and GeTe were calculated up to 12-fold ring, as shown in Fig. 2(a). In the case of Ge$_2$Sb$_2$Te$_5$ crystal, 20% of vacancy in Ge/Sb mixing site produces about 20% of sixfold rings. It is remarkable that $a$-Ge$_2$Sb$_2$Te$_5$ can be regarded as “even-numbered ring structure,” because the ring statistics is dominated by four- and six-fold rings analogous to the crystal phase. On the other hand, we find that $a$-GeTe has various size (both odd- and even-numbered) rings due to the formation of Ge–Ge homopolar bonds. These differences in the network of the ring structure are clearly visible in three-dimensional atomic configurations obtained from the RMC simulation, as shown in Fig. 2(b).
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9The density gain during crystallization of the amorphous phase exhibits 5% (Refs. 7 and 10) in GeSb2Te5 and 14% (Refs. 8 and 11) in GeTe.

15We employed the cubic NaCl-type structure as the approximate initial configuration of our RMC simulation for amorphous GeTe due to the limitation of our RMC program. It is thought that this approximation is not unreasonable, because it is well known that rhombohedral GeTe exhibits slightly distorted NaCl structure.
16We derived the isotropic temperature factors B of the crystal of GeTe and GeSb2Te5 from Rietveld analysis. Magnitude of B of Ge (B=1.51 Å²) and Te (B=0.58 Å²) sites in GeTe is smaller than Ge/Sb (B=3.44 Å²) and Te (B=0.76 Å²) sites in GeSb2Te5, respectively. We suspect that this behavior is due to the large amount of the vacancies in GeSb2Te5.
17See EPAPS Document No. E-APPLAB-89-253645 for additional figures and table on the RMC model. This document can be reached through a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).

18Maeda and Wakagi found the formation of Ge–Ge homopolar bonds at around 2.48 Å in a-GeTe, which disappear during amorphous-crystal phase change (Ref. 19).

21The ring size distributions were calculated using the shortest-path analysis, where we count the number of atoms that exist in the count from an atom in the starting point and returning to the atom through the shortest path length in order to avoid the counting of a large-number fold ring that can be divided into smaller-number fold rings.
22Ring statistics in a-GeSb2Te5 is the result of the RMC simulation under the conditions that homopolar bonds (Ge–Ge and Sb–Sb) are not formed in a-GeSb2Te5, since the presence of the homopolar bonds have been denied (Ref. 4) and have not been confirmed from our experimental data of a-GeSb2Te5 (Figs. S1 and S3 in EPAPS (Ref. 17)).