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

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The three-dimensional atomic configuration of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe were derived by reverse Monte Carlo simulation with synchrotron-radiation x-ray diffraction data. The authors found that amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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 $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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 compound¹ and Yamada *et al.* on Au–Ge–Sn–Te in a single-phase structure.² They reported that these materials show a high-phase stability of the amorphous phase and a very short crystallization time. The pseudobinary compound $2\text{GeTe}-\text{Sb}_2\text{Te}_3$ ($\text{Ge}_2\text{Sb}_2\text{Te}_5$) (Ref. 3) is one of the well-established commercial materials for digital versatile disk–random access memory (DVD–RAM) device.

Recently, Kolobov *et al.*⁴ investigated the local coordination around the Ge, Sb, and Te atoms in both the crystal and the amorphous phases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ by means of the extended x-ray absorption fine-structure spectroscopy (EXAFS). They ascribed the crystal–amorphous/amorphous–crystal phase change by the term of the umbrella flip of the Ge atoms from the octahedral site to the tetrahedral site, which concluded that the transformation between the two sites is the reason for the fast optical switching of the DVD–RAM. However, the proposed model based on EXAFS data reveals only local structure of the amorphous phase: hence it is necessary to analyze the large-scale three-dimensional structure of the amorphous phase.

In this letter, we focused on amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (*a*- $\text{Ge}_2\text{Sb}_2\text{Te}_5$) (crystallization speed: 20 ns)^{5,6} and GeTe (*a*-GeTe), crystallization speed: 100 ns)¹ 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 $\text{Ge}_2\text{Sb}_2\text{Te}_5$ exhibits NaCl-type structure with 20% vacancy of Ge/Sb mixing site due to the pseudobinary system,⁷ and GeTe exhibits trigonal-type structure without vacancy.⁸ On the other hand, the structure of the amorphous phase in both materials is still unknown. However, small density (volume) change⁹ due to the large amount of vacancy in the crystal phase during the crystallization of the amorphous phase in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ suggests that *a*- $\text{Ge}_2\text{Sb}_2\text{Te}_5$ exhibits a unique amorphous structure. Therefore we derived the large-scale atomic structures of *a*- $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and *a*-GeTe using reverse Monte Carlo (RMC) simulation¹² on the high-energy synchrotron x-ray diffraction.

The detail of preparation of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe specimens is described elsewhere.⁷ The high-energy x-ray diffraction experiments were carried out at the SPring-8 beamline BL02B2 (Ref. 13) and BL04B2.¹⁴ The details of data analysis are described elsewhere.¹⁴ The RMC simulation was performed on an ensemble of 3686 and 4096 particles for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe, respectively, starting with the

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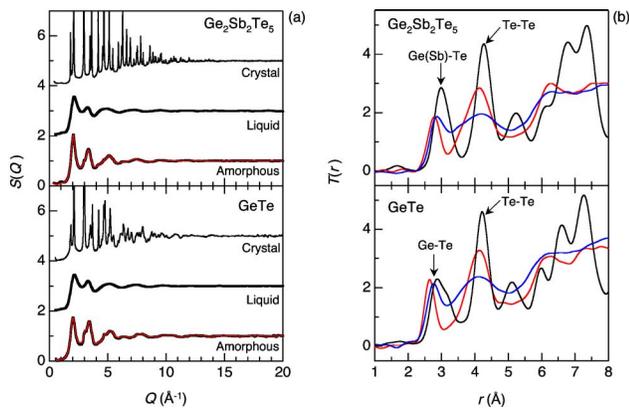


FIG. 1. (Color online) Total structure factors $S(Q)$ of crystal (300 K), liquid (953 K), and amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (300 K) and crystal (300 K), liquid (1073 K), and amorphous GeTe (a). Black lines and red lines represent the experimental data and the best-fitted result of the RMC simulation data, respectively. Total correlation functions $T(r)$ of crystal (black), liquid (blue), and amorphous (red) $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe (b).

NaCl-type configuration.¹⁵ Throughout the RMC simulation, the constraint of closest atom-atom approach was applied so as to avoid the appearance of unphysical spikes in the partial-pair distribution functions. The atomic number densities of $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ and $a\text{-GeTe}$ are chosen to be 0.0315 and 0.0337 \AA^{-3} , respectively, which are consistent with the reported data.^{10,11} In addition, we started with a random configuration, which led us to almost the same atomic arrangement of the amorphous phase.

Figure 1(a) shows the measured structure factors $S(Q)$. The diffraction pattern of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe crystals consists of sharp Bragg reflections, indicating the long-range periodicity in the atomic arrangement.¹⁶ On the other hand, the diffraction patterns of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (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 $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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 \AA 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 $\text{Ge}_2\text{Sb}_2\text{Te}_5$ 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 $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ and $a\text{-GeTe}$ 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

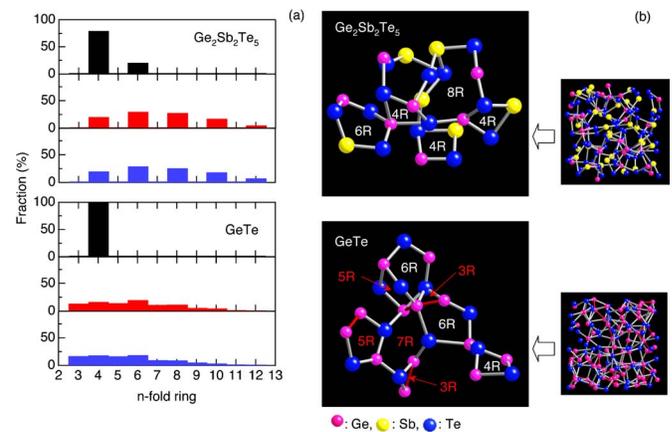


FIG. 2. (Color online) Ring size distribution in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe (a). Black, red, and blue bars represent the distribution in the crystals, amorphous (obtained by RMC simulation started with NaCl-type structure), and amorphous (obtained by RMC simulation started with random structure), respectively. A $16 \times 16 \times 16 \text{ \AA}^3$ atomic configuration and enlarged framework atomic configuration of $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ and $a\text{-GeTe}$ obtained from the RMC snapshot (b). The Ge(Sb)–Te and Ge–Ge bonds shorter than 3.4 and 3.0 \AA are indicated by the sticks, respectively. The red-colored bond represents the Ge–Ge bond.

distribution of the Ge–Te and Sb–Te distances from 2.4 to 3.4 \AA due to highly distorted structural units. Furthermore, the formation of Ge–Ge homopolar bond¹⁸ in $a\text{-GeTe}$ is confirmed in $g_{ij}(r)$ of Ge–Ge, whereas the formation of Ge(Sb)–Ge(Sb) bonds in $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ 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 $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ 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 .²⁰ Te–Ge–Te in $a\text{-GeTe}$ 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 $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ possesses a crystal-like bond angle order, whereas $a\text{-GeTe}$ 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 $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ and around the Ge is 4.1 for $a\text{-GeTe}$. Therefore it is suggested that dominant short-range structural units are GeTe_4 and SbTe_3 for $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$, and GeTe_4 and GeTe_3Ge for $a\text{-GeTe}$.

The ring statistics²¹ for the amorphous and crystal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe were calculated up to 12-fold ring, as shown in Fig. 2(a). In the case of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ crystal,⁸ 20% of vacancy in Ge/Sb mixing site produces about 20% of sixfold rings. It is remarkable that $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ can be regarded as “even-numbered ring structure,” because the ring statistics is dominated by four- and six-fold rings²² analogous to the crystal phase. On the other hand, we find that $a\text{-GeTe}$ 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).

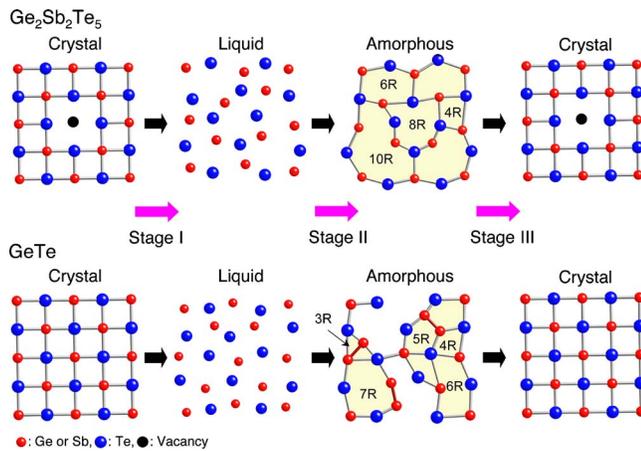


FIG. 3. (Color online) Schematic presentation for the possible ring size transformation in crystal-liquid-amorphous phase change (record) and amorphous-crystal phase change (erase) in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe . The red-colored bond represents the Ge-Ge bond. Stage I and II: recording process and stage III: erasing process.

From the comparison of the ring statistics, the mechanisms of fast crystal-liquid-amorphous (record) and amorphous-crystal (erase) phase changes in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are proposed by the schematic presentation, as shown in Fig. 3. In the crystal-liquid phase-change process (stage I), atomic configuration in the crystal phase is disarranged by the laser heating and melted in liquid, where there is no significant structural difference between $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe (see also Fig. 1). Meanwhile in the liquid-amorphous phase-change process (stage II), only even-numbered rings are constructed in $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$. In the amorphous-crystal phase-change process (stage III), $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ can transform to the crystal phase with only the transformation of the large-size even-numbered (8-, 10-, 12-fold) rings to NaCl-type structure (4- and 6-fold rings) with forming Ge(Sb)-Te bonds and without breaking bonds. On the other hand, $a\text{-GeTe}$ exhibits various size (both odd- and even-numbered) rings in stage II due to the formation of Ge-Ge homopolar bonds. Therefore the recombination of the various size rings attended with breaking of Ge-Ge homopolar bonds and with forming of Ge-Te bonds is required in stage III, since odd-numbered rings can be transformed into even-numbered rings with breaking of Ge-Ge bonds. Thus the construction of odd-numbered rings induced by the formation of Ge-Ge homopolar bonds in $a\text{-GeTe}$ disturbs the fast crystallization of the amorphous phase, and it is worth mentioning that the addition of Sb atom to GeTe can effectively prevent the formation of Ge-Ge bonds in $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$.

In conclusion, we found that the ring statistics of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is dominated by four- and sixfold rings analogous to the crystal phase, by means of the RMC analysis. We believe that such an unusual ring statistics of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ is the key for the fast crystallization speed of the material.

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⁹The density gain during crystallization of the amorphous phase exhibits 5% (Refs. 7 and 10) in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and 14% (Refs. 8 and 11) in GeTe .

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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 $\text{Ge}_2\text{Sb}_2\text{Te}_5$ from Rietveld analysis. Magnitude of B of Ge ($B=1.51 \text{ \AA}^2$) and Te ($B=0.58 \text{ \AA}^2$) sites in GeTe is smaller than Ge/Sb ($B=3.44 \text{ \AA}^2$) and Te ($B=0.76 \text{ \AA}^2$) sites in $\text{Ge}_2\text{Sb}_2\text{Te}_5$, respectively. We suspect that this behavior is due to the large amount of the vacancies in $\text{Ge}_2\text{Sb}_2\text{Te}_5$.

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 $a\text{-GeTe}$, which disappear during amorphous-crystal phase change (Ref. 19).

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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 $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ is the result of the RMC simulation under the conditions that homopolar bonds (Ge-Ge and Sb-Sb) are not formed in $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$, since the presence of the homopolar bonds have been denied (Ref. 4) and have not been confirmed from our experimental data of $a\text{-Ge}_2\text{Sb}_2\text{Te}_5$ [Figs. S1 and S3 in EPAPS (Ref. 17)].